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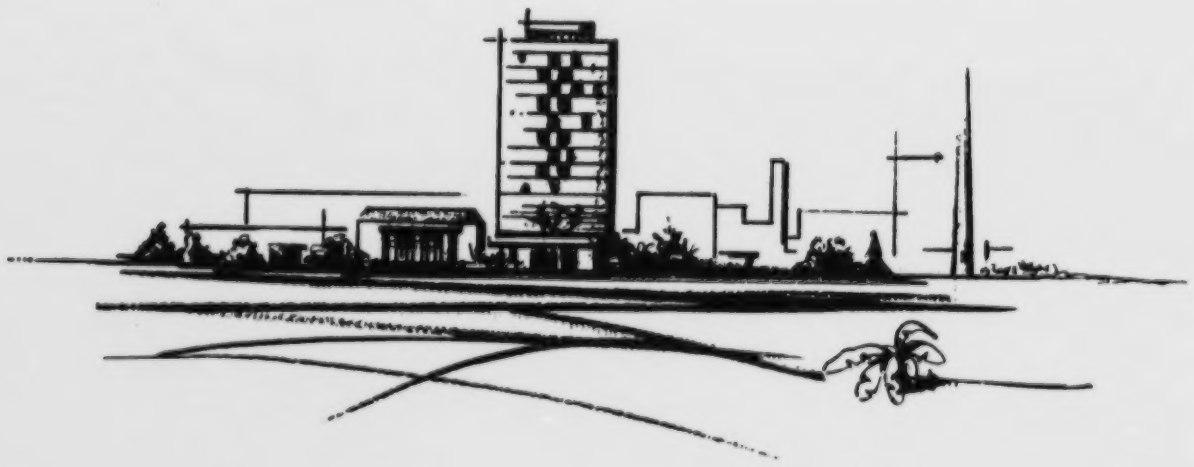

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SUMMARY REPORT

on

INVESTIGATION OF THE REACTIVITY OF LIMESTONE AND DOLOMITE FOR CAPTURING SO_2 FROM FLUE GAS

to

NATIONAL AIR POLLUTION
CONTROL ADMINISTRATION

June 27, 1969

by

R. W. Coutant, B. Campbell, R. E. Barrett,
and E. H. Lougher

Contract No. PH 86-67-115

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TABLE OF CONTENTS

	Page
INTRODUCTION	1
SUMMARY	1
Experimental Results	1
Conclusions and Recommendations	2
EXPERIMENTAL DETAILS	3
Materials Preparation and Analysis	3
Particle Sizing	3
Calcination and Hydration	4
Chemical Analyses	4
Results and Discussion	6
General Characteristics of SO_2 Reaction	6
Effect of SO_2 Concentration	9
Effect of Particle Size	11
Effect of Chemical State of Stone	15
Effect of Temperature	15
Recommended Future Work	20
APPENDIX A	
DISPERSED-PHASE REACTOR	A-1
APPENDIX B	
SPECTROCHEMICAL ANALYSIS OF STONES	B-1
APPENDIX C	
REACTOR DATA	C-1
APPENDIX D	
TREATMENT OF DATA	D-1
APPENDIX E	
TEMPERATURE DEPENDENCE OF RATE DATA	E-1
APPENDIX F	
INVESTIGATION OF TVA STONES	F-1

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INTRODUCTION

This investigation, conducted under Contract No. PH 86-67-115, is concerned with some of the fundamental aspects of the reactivity of limestones and dolomites with SO_2. Work done under the first segment of this program has been reported in the Summary Report* dated August 30, 1968. The purpose of the current work was to extend the measurements of the rate of reaction of several limestone-based materials with SO_2 under varied conditions of SO_2 concentration, temperature, particle size, and solid composition so as to develop further understanding of the nature of physicochemical processes that are important to utilization of limestone as an agent for SO_2 removal from flue gas. This Summary Report covers work done on the program during the period July 1, 1968, through February 28, 1969.

SUMMARY

Experimental Results

The reaction of SO_2 with limestones, dolomites, and limes was studied under simulated boiler conditions with the dispersed-phase reactor.** This reactor provides for injection of limes or stones into a flue-gas stream. As in the case of injection into a power boiler, the particles are dispersed in the gas; also, as in a boiler, the samples are near room temperature when injected, and must heat up (and calcine in the case of raw stones) before reacting with the SO_2 present. Conditions differ from those in a boiler in that the walls are kept hot to maintain relatively constant gas temperature, and the samples are small compared with the amount of gas so that the SO_2 level remains essentially constant.

For the experiments conducted, gas temperatures were between 1300 and 2100°F and residence times were from 0.1 to 0.5 seconds at 2100°F and from 0.4 to 2.1 seconds at the lowest temperature. The highest calcium utilization observed under the conditions employed was about 27 percent. In general, the reaction with raw stones is

*Summary Report on "Investigation of the Reactivity of Limestone and Dolomite for Capturing SO_2 From Flue Gas", to National Air Pollution Control Administration, August 30, 1968.

**See Appendix A for description.

characterized by incomplete calcination within all but the longest residence times at the highest temperatures when -140 + 200 U. S. Standard mesh stone is used. Concurrent with the calcination process is the formation of calcium sulfite and calcium sulfate. It was found that sulfite is the predominant form of sulfur at short residence times and that the fraction of sulfur present as sulfite can be correlated with the degree of calcination.

A study of the effect of particle size on the apparent rate of reaction at 1900°F and 0.5 second for two limestones, Nos. 1683 and 1373*, and two dolomites, No. 1337 and Basic Chemicals, Inc., dolomite, suggested an inverse relationship between size and reactivity as average particle size was varied from 130 to about 50 microns. With smaller particles (down to 5 to 10 microns), the results were somewhat erratic, but no significant further increase in reactivity was apparent. This trend can be explained at least partly on the basis of the rate of heatup of the particles and the nature of the initial chemical reactions.

Investigation of the effect of SO_2 concentration on the apparent reaction rate of No. 1359 and the Basic Chemicals dolomite at 2000°F and 0.12 second showed reactivity increasing with concentration up to about 0.1-0.2 volume percent SO_2 but no significant increase in reactivity at higher concentrations. It is believed that this observation can also be explained in terms of transport processes.

The current results suggest that the hydrated limes may have a peak reactivity in the neighborhood of 2000°F. For No. 1337, a dolomite, the dihydrate is the most reactive form in the temperature range studied, with the order of reactivity being dihydrate > raw stone > monohydrate > burnt lime. For No. 1359, a high-purity limestone, the order of reactivity is raw stone > hydrate > burnt lime.

Apparent activation energies for SO_2 reaction, obtained from Arrhenius plots of the data, ranged from about 11 to about 28 kcal/mole for the various stones and burnt limes studied.** Because of the complexity of the reaction process, and because gas temperatures rather than the unknown reaction temperatures are used in the Arrhenius plots, the activation-energy values obtained should not be considered as indicative of any specific chemical or physical processes, but rather as overall trends in the data.

Conclusions and Recommendations

The overall reaction between raw stones and SO_2 in the reactor follows a complex path, the nature of which is due in part to the slow heatup of stone particles as a result of the thermal requirements for calcining the stone. Sulfite formation is the primary mode of sulfur pickup during the early stages of the process, during which time the stone is still relatively cool. In later stages of the process, as the stone heats up to temperatures above the thermodynamic limit for sulfite existence (about 1400°F), the sulfite can calcine and sulfur is lost from the particles. Concurrent with these steps, the sulfite can be oxidized and/or disproportionate to form sulfate and sulfide. The net result, however, is a maximum in sulfur pickup during the first second of exposure in the reactor. The time required for attainment of this maximum and the magnitude of the maximum pickup are likely to depend upon factors which influence the

*Stone numbers used in this report are those used by NAPCA and other NAPCA contractors.
**Values were not obtained for the hydrates, since the data did not fit an exponential relationship.

heatup time and the rate of oxidation or disproportionation, e.g., particle size, injection temperature, oxygen pressure, the duration of exposure at a given temperature, and the details of the physical state of the lime formed during the calcination step. If, for example, injection in a boiler is made at very high temperatures (>> 2300°F) and in a region of the boiler where temperature does not change rapidly with time, then heatup, calcination, and sulfite formation and decomposition might take place within such a short time scale that the maximum in the sulfur pickup curve might be undetectable and relatively unimportant in the overall process. On the other hand, if injection in the boiler is made near the superheater section where the gas temperature begins to drop off very rapidly, calcination may not be complete within the time available, and sulfite may be the principal product of sulfur pickup. However, this effect would be reduced with the use of very small particles because of their rapid heatup.

The results of the current work provide at least a qualitative understanding of the overall reaction trajectory of the limestone-SO_2 reaction and a possible connection between the results of the relatively long-term experiments carried out by NAPCA and others and the short-term exposure in the dispersed-phase reactor or in a boiler. A detailed set of recommendations directed toward further clarification of the limestone-SO_2 reaction has been submitted to NAPCA. In essence, on the basis of the results obtained in this program, it is recommended that consideration be given to a detailed fundamental study of the calcination and SO_2 reaction for short residence times such as would be encountered in a boiler, with the goal of elucidating the importance of heat transport, mass transport, and chemical reaction rate to the overall sequence of events occurring when limestone is injected into flue gas.

EXPERIMENTAL DETAILS

In the current series of experiments, study of the reaction between limestone-based materials and SO_2 was continued using the dispersed-phase reactor. Results of the previous work, along with details of construction and operation of the reactor are given in the Summary Report dated August 30, 1968. A brief description of the reactor also is presented in Appendix A. In this reactor, sized particles of stone, burnt lime, or hydrated lime are injected into a nearly isothermal stream of flue gas and are transported by the gas stream to a collection probe, whence they are withdrawn from the flue gas for chemical analysis. Residence time in the reactor is determined by probe spacing and gas-stream velocity. The samples are small compared with the volume of gas to which they are exposed, so the particles encounter essentially constant SO_2 concentration throughout the run. The nominal gas temperature reported for the reaction is that on the centerline at a point midway between the injection and collection probes.

Materials Preparation and Analysis

Particle Sizing

For the most part, the samples of stones and limes used in this study were -140 + 200 U. S. Standard mesh, obtained by grinding and sieving bulk samples provided

by NAPCA. For the particle-size study, the three larger sizes, -100 + 120, -140 + 200, and -270 + 325 U. S. Standard mesh, were sieved with wire-mesh screens. For the three smaller sizes, 20-40, 10-20, and 5-10 microns, electroformed screens were used.

Calcination and Hydration

Specimens were calcined in a laboratory rotary kiln under conditions specified by the Sponsor: 2 hours at 1800°F in flowing nitrogen. A stainless steel kiln, lined with pyrophillite (a refractory ceramic) to prevent reaction of the limes with the metal-oxide surface of the kiln, was used for the calcination. The same kiln was used with a Pyrex liner for preparing the hydrated limes. A schematic drawing of the hydration apparatus is shown in Figure 1.

Conventional laboratory procedures for hydration of limes involve addition of liquid water to the lime. Because of the strongly exothermic nature of the reaction, this type of hydration is normally quite violent and causes disruption of the burnt-lime particles. In the current work it was desired to retain original particle size so that comparison of the reactivity of hydrated limes with that of burnt limes could be made without change in relative particle size. The following procedure for hydration was adopted. The lime is first heated to about 660°F and steam is admitted to the kiln at a pressure of 1 atmosphere. The temperature of the kiln is then allowed to decrease gradually over a period of several hours to 230 to 250°F while steam is admitted continuously. With this procedure, the rate of hydration is kept low and disruption of the lime particles is minimized. After completion of the temperature program, dry nitrogen is passed over the lime to remove any excess water from the kiln. The resultant limes are dry powders having approximately the same particle-size range as the original stone, as indicated by sieving, and containing stoichiometric quantities of water, as judged by thermogravimetric analyses of the products. Because of the resistance of MgO to hydration, only the calcium oxide portion of a lime is hydrated by this method. However, substantial fractions of the MgO in a dolomitic lime can be hydrated by increasing the steam pressure. By maintaining steam pressure at 80 to 90 psi and lime temperature at 300 to 320°F for 12 hours, a sample of dihydrated No. 1337 was prepared in which 80 percent of the MgO was hydrated. This material was used in experiments with dihydrated lime.

Chemical Analyses

Reacted specimens obtained from the dispersed-phase reactor were analyzed for total sulfur, calcium, and magnesium content, and selected specimens also were analyzed for sulfite content. Both calcium and magnesium were determined by atomic-absorption photometry. Total sulfur was determined as $CaSO_4 \cdot 2H_2O$ by the wet-chemical method outlined in the Summary Report dated August 30, 1968. An essential step in this procedure is the oxidation of non-sulfate sulfur to sulfate using hydrogen peroxide. Sulfite analysis was made by the same procedure, but the oxidation step was not performed. Instead, the solution of the reacted specimen was swept with nitrogen to remove SO_2. The remaining sulfate was then determined in the usual manner and the sulfite content was obtained by difference. The accuracy of the method has not been tested. No analyses for sulfide were made.

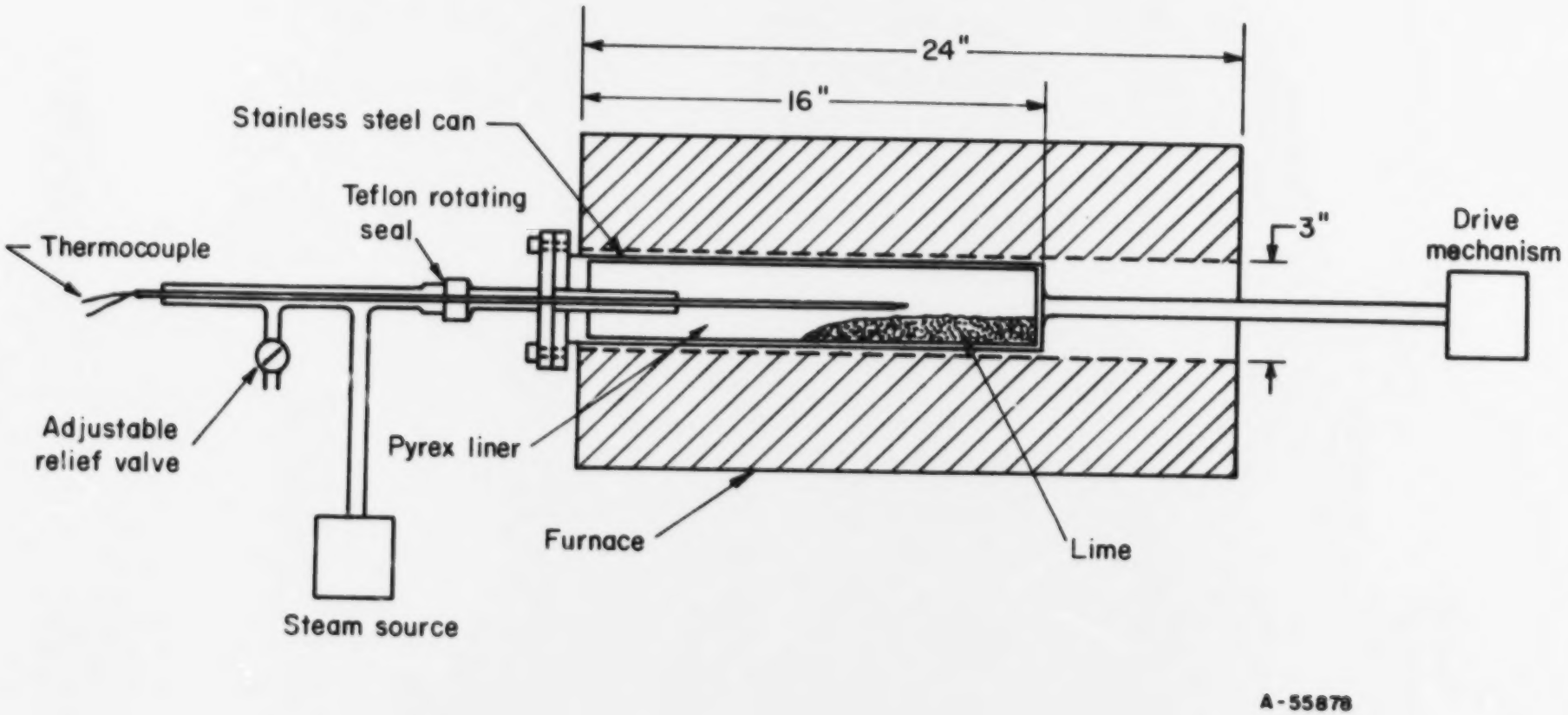

FIGURE 1. KILN, ADAPTED FOR HYDRATION

Analytical data for most of the limes were supplied by Bituminous Coal Research, Inc., and are given in Appendix B. Two new stones used in the current work, the Basic Chemicals dolomite and the TVA (Colbert County) limestone, were analyzed for calcium content by atomic-absorption photometry. The burnt limes obtained from these stones were found to contain 61 and 95 weight percent CaO, respectively.

Results and Discussion

A complete listing of experimental conditions, analytical results, calculated values of reactivity, and percentage calcination for all runs made on this segment of the program is given in Table C-1 in Appendix C. Data displayed in tables and figures discussed below are abstracted from this table. Mathematical procedures for calculation of reactivity and percent calcination are given in Appendix D.

General Characteristics of SO_2 Reaction

All of the stones and limes were reacted for three residence times at each of several temperatures. At temperatures between 1500 and 2100°F the qualitative features of the observed reaction trajectory were the same for all materials. The total sulfur content of samples exposed for the longest residence time at a given temperature was lower than that found in the same material exposed for the intermediate residence time.* In some cases, there was even less sulfur in the long-residence time samples than in those exposed for the shortest period. That is, for all materials, a definite maximum in sulfur pickup was observed within the range of residence times used in the reactor.

It was also found, for -140 + 200 mesh stone, that calcination is generally incomplete during the exposure in the reactor, except for experiments at the longest residence times at the highest temperatures.

Selected samples of several reacted stones were analyzed for sulfite as well as for sulfate content. The results of these measurements are shown in Table 1. It can be seen that sulfite is the predominant form of sulfur for runs made at the shortest residence times and lowest temperatures, whereas sulfate is predominant only for longer residence times at higher temperatures. The presence of sulfite at gas temperatures above the thermodynamic stability point of the sulfite, about 1400°F, suggests that an appreciable part of the residence time in the reactor is consumed before particle temperature approaches gas temperature. Figure 2, plotted from data in Table 1, shows that the fraction of the sulfur as sulfite is also related to the degree of calcination, suggesting either that one process controls the other or that the rates of calcination and sulfite formation are related through a common mechanism.

*For example, see Figures 8 and 9.

TABLE 1. SULFITE ANALYSES

Sample No.	Stone No.	Particle Size[a]	Temp, °F	Residence Time, sec	Total S[b]	$SO_3^=$[b]	$SO_3^=/S$	Percent Calcination[c]
10-24-L	1683	-140+200	1800	0.58	18.6	9.7	0.52	51
11-1-E	1683	-140+200	1800	0.18	5.9	3.9	0.66	32
1-28-R	1683	-140+200	1800	0.95	11.4	2.7	0.24	92
10-30-L	1683	-140+200	2000	0.34	15.3	1.5	0.098	83
11-7-E	1683	-140+200	2000	0.10	4.1	0		
11-19-A	1683	-140+200	2000	0.50	13.4	2.4	0.18	79
1-13-D	1683	20-40 μ	1900	0.51	15.7	1.8	0.11	96
1-13-L	1683	10-20 μ	1900	0.51	21.1	5.5	0.26	87
1-13-Y	1683	5-10 μ	1900	0.51	23.7	4.8	0.20	92
10-18-C	1683	-100+120	1900	0.47	11.2	7.4	0.66	81
10-18-E	1683	-140+200	1900	0.47	14.1	8.3	0.59	91
10-18-L	1683	-270+325	1900	0.47	16.9	6.6	0.39	87
10-28-C	1337	-140+200	2000	0.40	25.3	6.2	0.25	73
10-28-D	1337	-140+200	2000	0.40	27.0	8.3	0.31	84
11-6-A	1337	-140+200	2000	0.12	12.5	7.5	0.60	56
11-6-B	1337	-140+200	2000	0.12	11.8	5.9	0.50	55
1-6-J	1337	-140+200	2000	0.61	22.1	2.9	0.13	106
1-6-K	1337	-140+200	2000	0.61	22.8	2.8	0.12	107
11-4-E	TVA	-140+200	1800	0.18	7.2	4.0	0.55	23
11-4-F	TVA	-140+200	1800	0.18	5.6	3.3	0.57	25
11-24-N	TVA	-140+200	1800	0.58	21.5	8.6	0.40	62
11-7-M	TVA	-140+200	2100	0.10	4.1	1.0	0.24	19
11-19-1	TVA	-140+200	2100	0.50	13.0	2.8	0.22	87
1-28-V	TVA	-140+200	1800	0.95	15.0	4.6	0.31	76
1-28-W	TVA	-140+200	1800	0.95	15.3	4.4	0.29	73

(a) U. S. Standard mesh, except as indicated.
(b) Expressed as weight percent $CaSO_4 \cdot 2H_2O$.
(c) Calculated percent calcination.

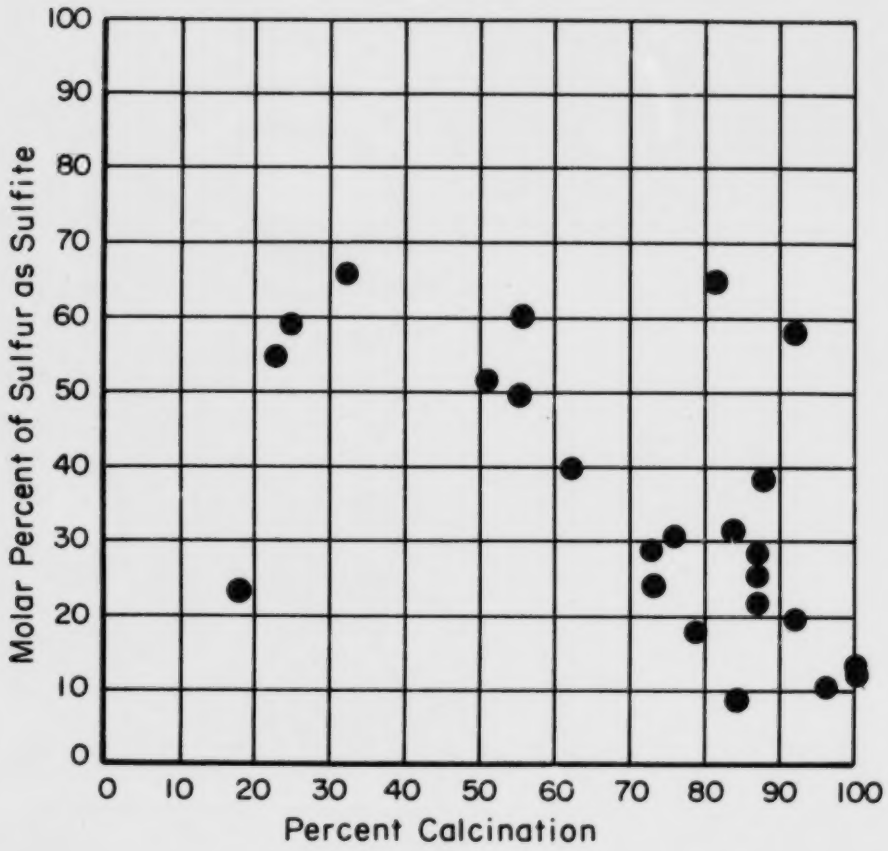

FIGURE 2. MOLAR PERCENTAGE OF SULFUR OCCURRING AS SULFITE AS A FUNCTION OF PERCENTAGE CALCINATION

The following mechanism is hypothesized as being consistent with these general experimental observations:

(1) The initial temperature of a particle of stone injected into the reactor is low relative to the temperature of the gas.

(2) The time required to heat a particle essentially to gas temperature is not negligible compared with its total residence time in the reactor. The length of this heating period depends partly upon the kinetics and heat of reaction of the calcination process. Thus, for example, raw stone heats up more slowly than burnt lime because of the endothermic calcination reaction.

(3) In calcination, while the particle is still at relatively low temperature, SO_2 begins to react with the lime forming calcium sulfite, which may gradually oxidize and/or disproportionate to $CaSO_4$ and CaS.* That is,

*The work of K. H. van Heek and H. Juntgen (discussed at the Third Limestone Symposium, St. Petersburg, Florida, December 4-8, 1967) and of S. Sprung in Schriftenreihe der Zimentindustrie 31, 1-67 (1964), indicates direct reaction of SO_2 with uncalcined limestone. However, the conditions employed in their work were quite different from those in the work reported here, and the results cannot be directly related.

$$CaO + SO_2 \rightarrow CaSO_3;$$

$$\text{then } CaSO_3 + 1/2O_2 \rightarrow CaSO_4$$

$$\text{and } 4CaSO_3 \rightarrow CaS + 3CaSO_4 \ .$$

(4) As the temperature of the particle continues to increase approaching gas temperature, some of the sulfite decomposes to yield SO_2 and free lime. At the same time, disproportionation and/or oxidation of the remaining sulfite may continue at an increased rate.

(5) Once the particle achieves gas temperature (above the decomposition point of the sulfite), the reaction continues at a new rate with SO_2 and O_2 to yield sulfate:

$$CaO + SO_2 + 1/2O_2 \rightarrow CaSO_4 \ .$$

According to this hypothesis, the initial reaction rate should be essentially characteristic of formation of sulfite at reduced temperatures. The total sulfur content may then go through a maximum before the characteristic high-temperature formation of sulfate commences. Work at NAPCA* and TVA**, as well as earlier work at Battelle***, has indicated lower rates of SO_2 sorption than those reported here. This may be a result of the longer term experiments employed in these studies; the maximum pickup point may have been passed in the course of the experiments, giving a lower average rate.

Effect of SO_2 Concentration

The effect of the concentration of SO_2 in the flue gas on the apparent reaction rate was studied using a limestone, No. 1359, and the Basic Chemicals dolomite (-140 + 200 U. S. Standard mesh). Exposure in the dispersed-phase reactor was at a mean gas temperature of 2000°F for a residence time of 0.12 second. Concentrations of SO_2 employed ranged from 100 ppm to about 6000 ppm; the amount of reaction at 100 ppm was too slight to be measurable.

The effect of changing concentration on the reactivities of the two stones is shown in Figures 3 and 4. Data used in constructing these plots are taken from the Summary Report of August 30, 1968, as well as from the current data. The behavior noted in Figures 3 and 4 is at variance with the linear dependence indicated by the preliminary data given in the above-mentioned Summary Report. Although there is considerable scatter in the data, it is clear that there is little dependence on concentration except at very low SO_2 levels. This fact is consistent with the notion that the rate of reaction is not controlled by the chemical reaction rate or the rate of admittance of SO_2 to the particle during the early reaction stages, but rather depends upon the availability of lime for reaction, i.e., on the calcination rate, which in turn may depend upon the rate of heat transfer to the particle.

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*R. H. Borgwardt, "Kinetics of the Reaction of SO_2 With Calcined Limestone", presented at Symposium on Limestone-Sulfur Dioxide Reaction Kinetics and Mechanisms, Cincinnati, Ohio, February 5-6, 1969.

**R. C. Mullins and J. D. Hatfield, "Effects of Calcination Conditions on the Properties of Lime", presented at the Symposium on Lime, Annual Meeting of ASTM, Atlantic City, New Jersey, June 23-27, 1969.

***Summary Report, August 30, 1968.

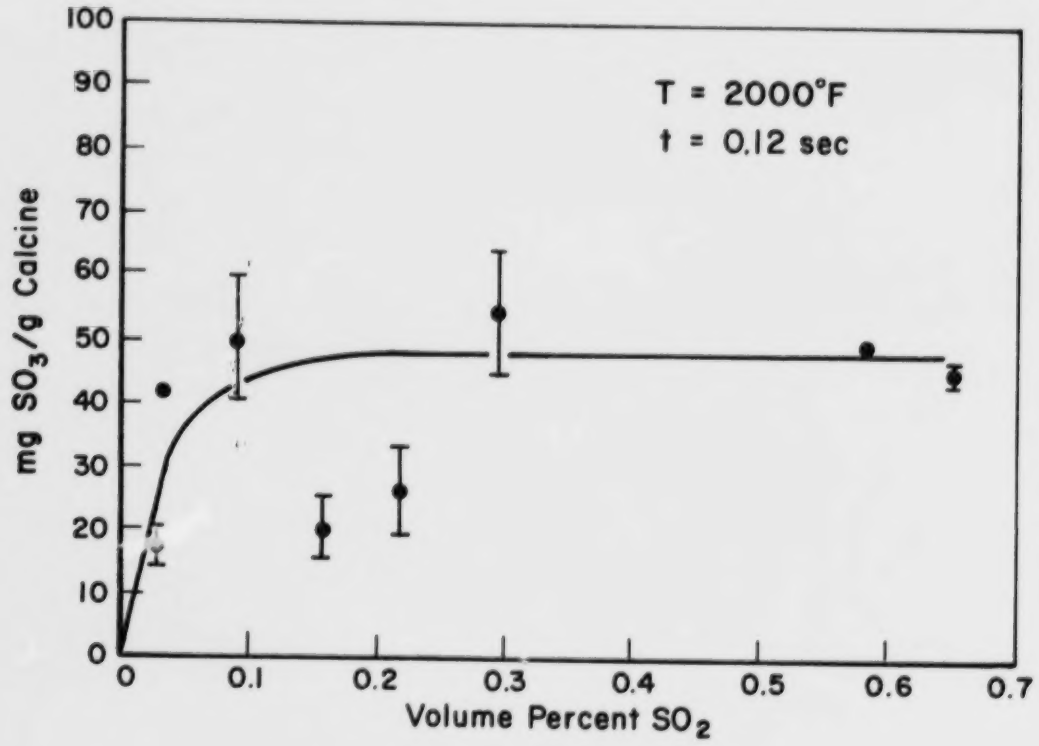

FIGURE 3. EFFECT OF SO_2 CONCENTRATION ON REACTIVITY OF NO. 1359 LIMESTONE

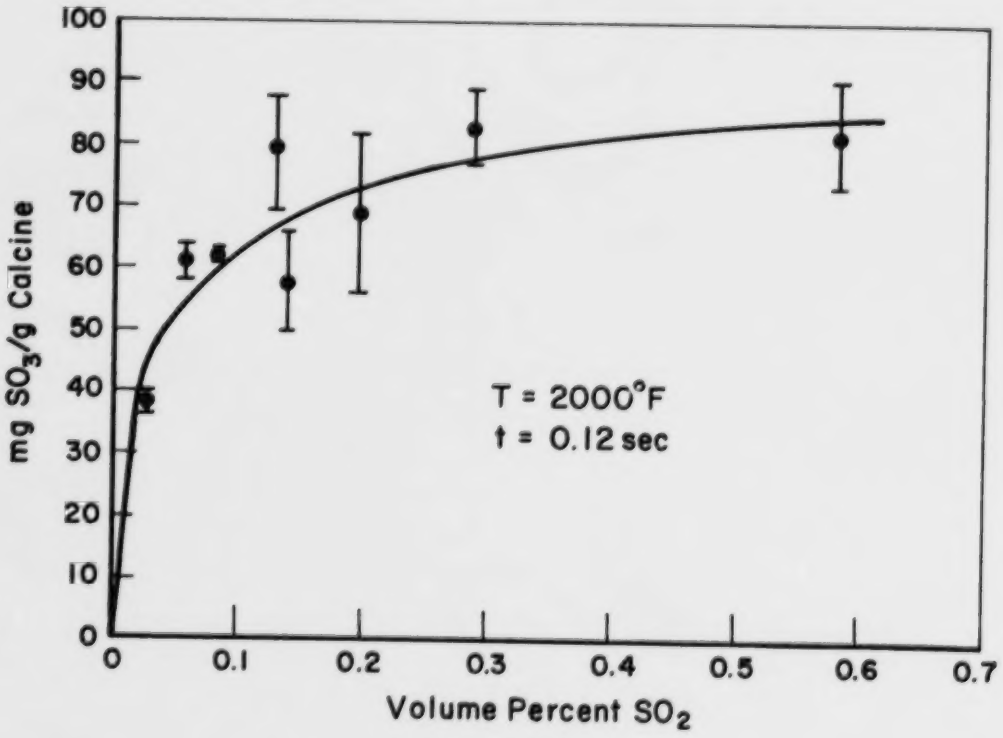

FIGURE 4. EFFECT OF SO_2 CONCENTRATION ON REACTIVITY OF BASIC CHEMICALS DOLOMITE

It is emphasized that the dependence shown in Figures 3 and 4 may not hold for reaction at the longer residence times of interest in boiler operation but is indicative only of the behavior during the initial portion of the reaction process. In fact, studies of SO_2 sorption at longer residence times have indicated a first-order dependence on SO_2 concentration.*

Effect of Particle Size

A study of the effect of particle size on the apparent rate of reaction of two limestones, Nos. 1373 and 1683, and two dolomites, No. 1337 and the Basic Chemicals dolomite, was carried out in the reactor at a gas temperature of 1900 F with a residence time of 0.5 second. Particle sizes used were 125-149, 88-105, and 44-53 microns (-100 + 120, -140 + 200, and -270 + 325 U. S. Standard mesh) and 20-40, 10-20, and 5-10 microns. For the four larger sizes noted, the sample injector used was the same as was used with all other runs made in the reactor.** However, this injector could not be used with the two smaller sizes because of agglomeration of the particles. A special injector, shown in Figure 5, was constructed for use with these small particles. With this injector, an appropriate amount of stone is placed in an airtight aluminum box which communicates with the reactor inlet through a short aluminum tube. The box is vibrated in line with the tube and reactor inlet, causing the particles to drift along the tube into a small mixing chamber wherein they are picked up by a stream of nitrogen and blown into the reactor. Rates of injection can be varied reliably through alteration of the amount of stone in the box and variation of the amplitude of vibration.

The effect of particle size on SO_2 pickup for the two limestones and two dolomites examined is shown in Figures 6 and 7. Contrary to preliminary estimates of the particle-size dependence***, the rate of reaction is not simply inversely proportional to particle size. This type of dependence may be a limiting case for the larger particle sizes, as indicated by the points for the three larger particle sizes on Figures 6 and 7, but with the smaller sizes there seems to be little or no dependence on size. It is also noted that there is considerable scatter in the data, particularly for the dolomitic stones. With these materials, especially No. 1337, extensive fragmentation was observed to accompany calcination of particles in the size range of -140 + 200 mesh. It may be that fragmentation is less pronounced with smaller particle sizes and that the size of particles actually taking part in the reaction with SO_2 was essentially independent of initial size. However, the limestones also show a leveling off of reactivity at the smaller particle sizes. Aggregation of the smaller particles into clusters may also be a factor.

These data for the effect of particle size on apparent rate of reaction are consistent with the sulfite-formation model discussed earlier. For smaller particles the rate of heatup should be greater than that of the larger particles, so that, for a given residence time, the smaller particles should be further along their respective reaction trajectories. Thus, the failure of the smallest particles to have high reactivity may indicate that they are further down the desorption side of the reaction curve. Possibly, their

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*Summary Report, August 30, 1968, Figure 7, and R. H. Borgwardt, op. cit.

**Summary Report, August 30, 1968, Figure 7.

***Summary Report, August 30, 1968, Figure 14. Increasing reactivity with decreasing particle size also is indicated by the investigation of K. M. Zentgraf, K. Tanaka, and Y. Ishihara (discussed at the Third Limestone Symposium, St. Petersburg, Florida, December 4-8, 1967) and by the work of R. C. Attig (Progress Report, December 10, 1968, Contract No. PH 86-67-127).

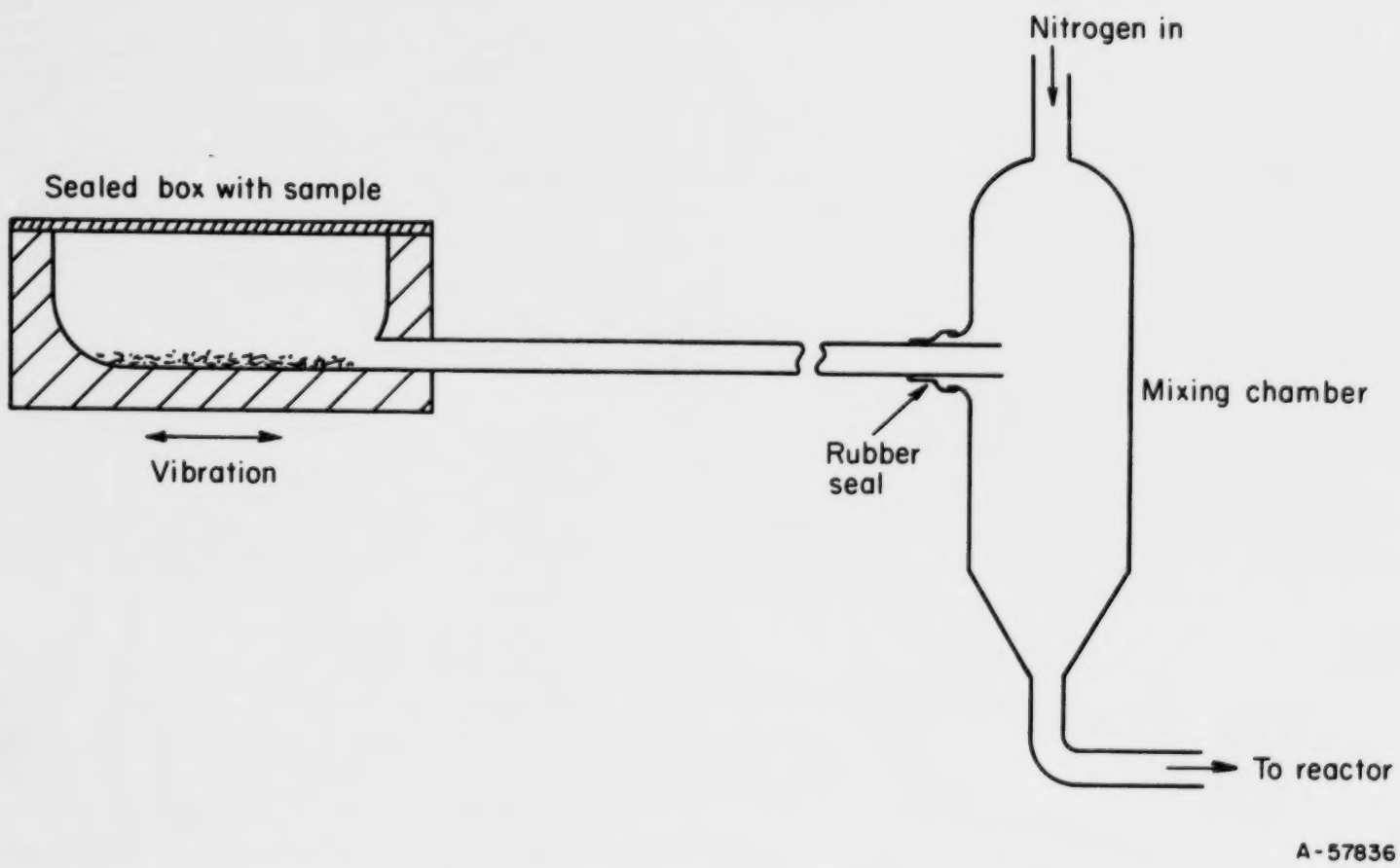

FIGURE 5. SMALL-PARTICLE INJECTOR

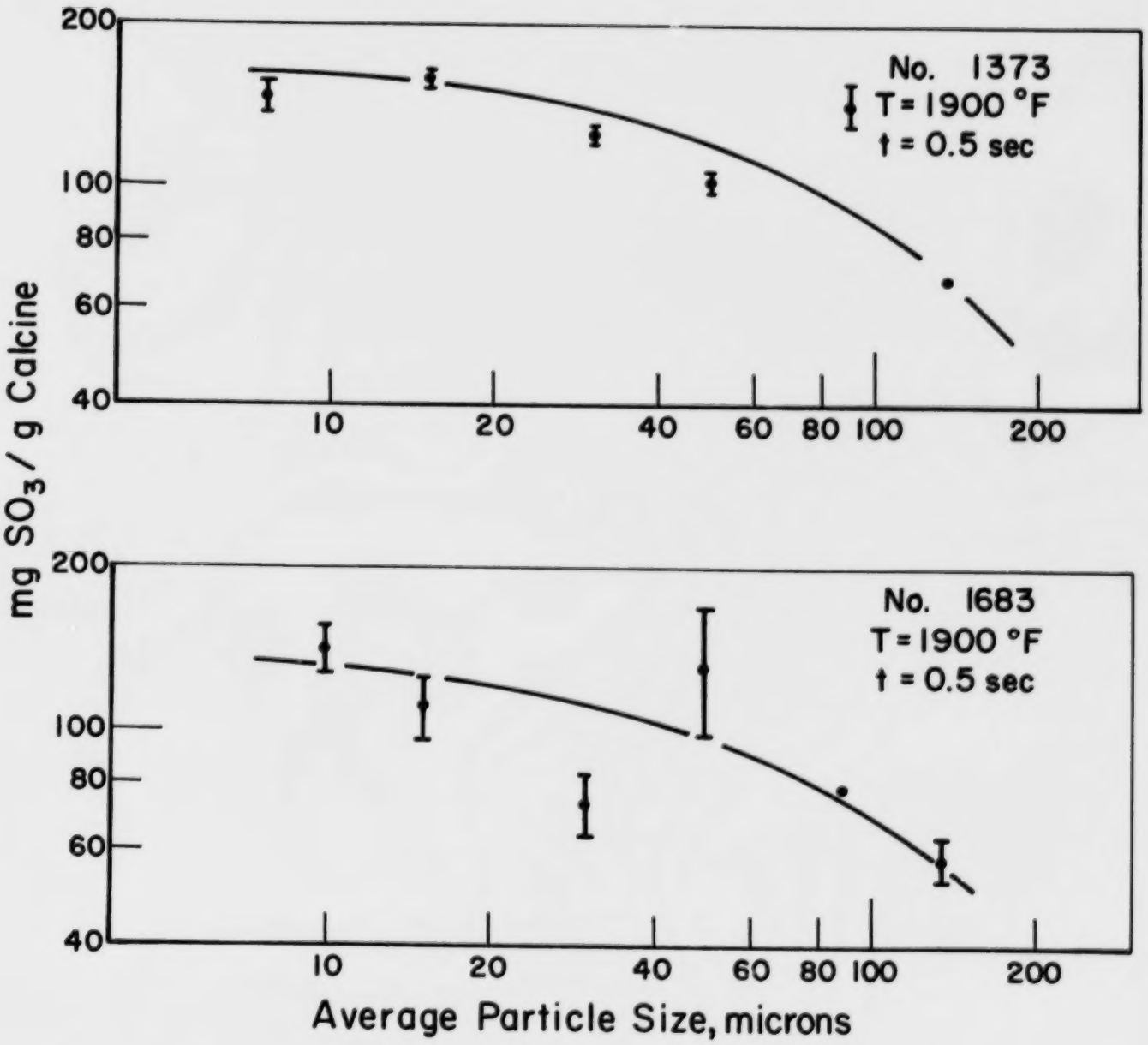

FIGURE 6. EFFECT OF PARTICLE SIZE ON REACTIVITY OF TWO LIMESTONES

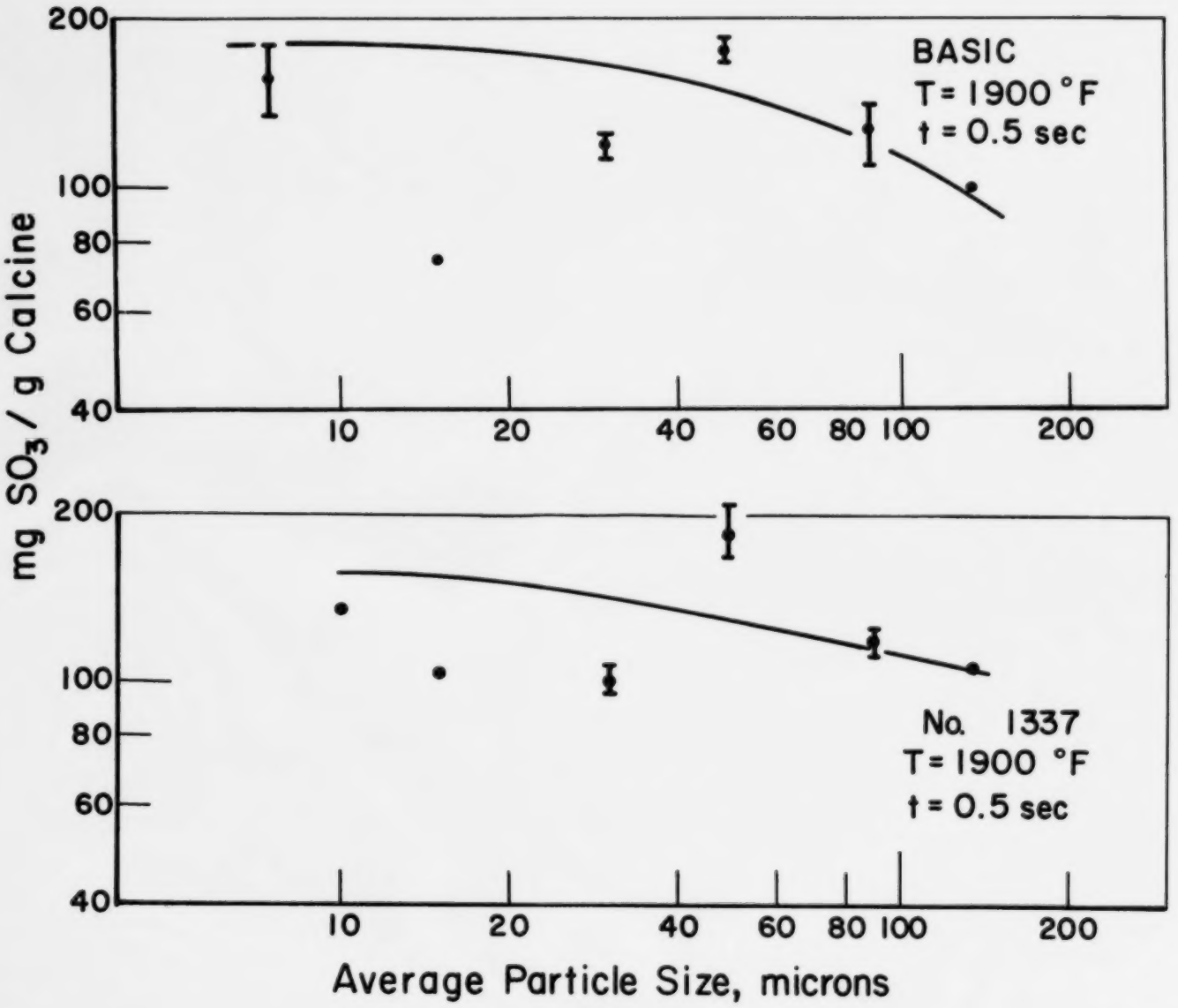

FIGURE 7. EFFECT OF PARTICLE SIZE ON REACTIVITY OF TWO DOLOMITES

reactivity would be greater than that of the larger particles for the longer residence times which would be used in a boiler, i.e., after SO_2 desorption has been completed and sulfate formation has become the dominant mode of sulfur pickup.

Effect of Chemical State of Stone

The question exists as to whether or not more efficient scrubbing of the SO_2 from flue gas can be achieved by injecting burnt or hydrated lime instead of raw stone. To explore this question, two stones were exposed in the reactor in different chemical forms at temperatures of 1500 to 2100°F. For limestone No. 1359, the reactivity of the burnt lime and hydrate was compared with that of the raw stone. For dolomite No. 1337, both the monohydrate and the dihydrate were studied, along with the burnt lime and raw stone. Special procedures outlined in the section on materials preparation were used to insure that the initial particle size was not a variable in these studies.

Figures 8 and 9 illustrate the results obtained at 2000°F. Qualitatively similar results were obtained at other temperatures. Regardless of residence time, the following order of reactivities was observed:*

Dolomite reactivity: dihydrate > raw stone > monohydrate > burnt lime
Limestone reactivity: raw stone > hydrate > burnt lime.

Scatter in the data does not permit quantitative conclusions on the relative efficacy of the various forms. However, over the temperature range used, the best materials were clearly the raw limestone and the dihydrate and raw stone in the case of the dolomite. Burnt lime was definitely inferior in both cases. A factor which may be partially responsible for the low ranking of the burnt lime is that this material was prepared by calcination for a long period of time – two hours at 1800°F – conceivably causing some sintering of the lime. The reason for the improved reactivity of the hydrates is not known; it may be related to the fact that the carbonate and hydrate have different crystal structures so that the CaO formed by calcination may, at least temporarily, have different structure or porosity in the two cases. With the dihydrate, there may be some additional fragmentation which occurs upon calcination, thus resulting in higher reactivity than for the raw dolomite, but no information concerning this point is available.

The data for the hydrates suggest a possible maximum in reactivity at about 2000°F. However, because of scatter in the data, the existence of a maximum cannot be established with certainty.

Effect of Temperature

The apparent reaction rate, i.e., the amount of SO_2 pickup per unit time, was determined at temperatures between 1300 and 2100°F for the various stones and limes examined in this program. Because of the complexity of the overall reaction process during exposure in the reactor, a true specific rate constant cannot be determined within

*Zentgraf, op. cit., found the order to be calcium hydrate > dolomite monohydrate > raw limestone > burnt lime (high calcium) for injection into a boiler at about 2100 F, but the ranking appeared to change with injection temperature. Also, his particle size was not the same for all specimens.

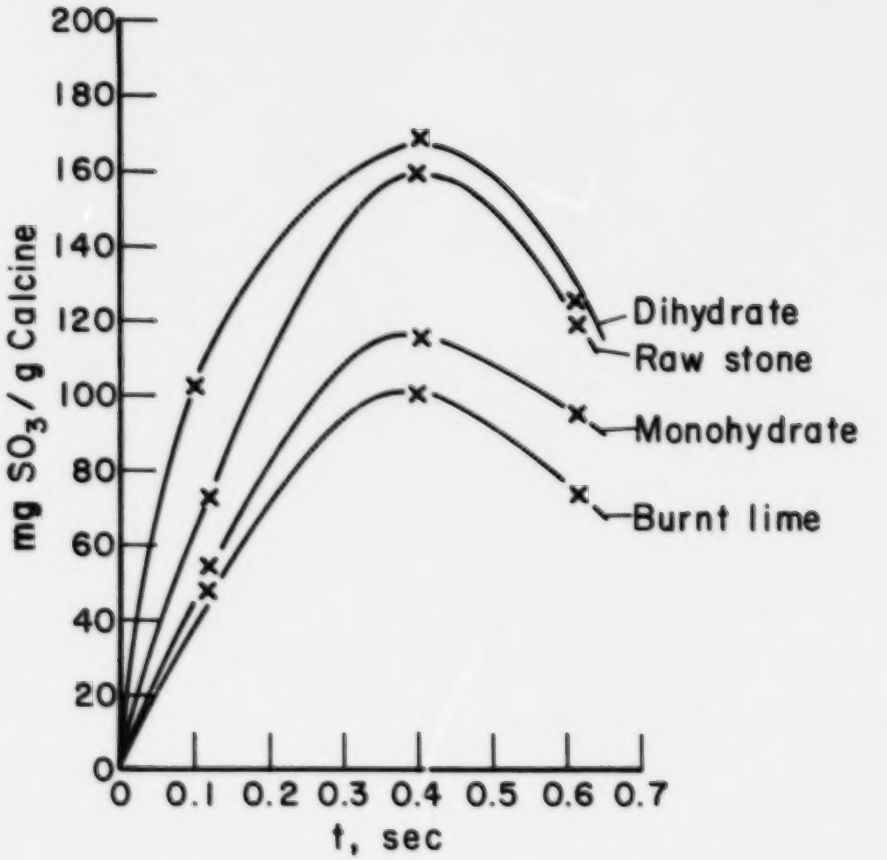

FIGURE 8. COMPARISON OF VARIOUS FORMS OF DOLOMITE NO. 1337 AT 2000°F

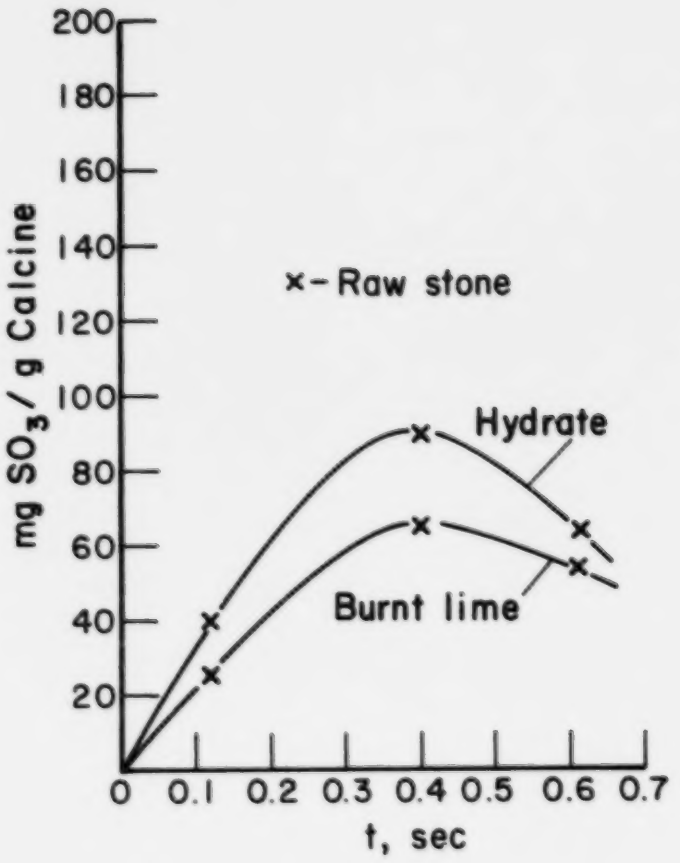

FIGURE 9. COMPARISON OF VARIOUS FORMS OF LIMESTONE NO. 1359 AT 2000°F

the limits of current understanding of the reaction process. Also, particle temperatures and, hence, true reaction temperatures probably are not well approximated by the mean gas temperature in the reactor. To the contrary, the actual reaction temperature undoubtedly varies considerably within the span of an exposure. If, as suggested above, the controlling mechanism in the overall process is heat transfer to and within the particles, the use of an Arrhenius-type equation, which applies strictly only to activated processes, is not entirely correct. However, Arrhenius plots are a convenient means for organizing the reaction-rate data and may provide useful comparisons of the reactivities of various materials.

Figures 10 and 11 show examples of Arrhenius plots, with lines fitted by least-square analysis, which were made for the various materials studied on this program, with the exception of the hydrates. (Plots for the remaining materials are presented in Appendix E.) As indicated above, the latter materials tend to display a maximum in reactivity as a function of temperature and, hence, cannot be approximated by an exponential relationship. Because of the complexity of the residence time-sulfur pickup relationship, three apparent rate curves, one for each residence time, were plotted for each temperature. These are identified in the figures by the subscripts S, M, and L, referring to short, medium, and long residence times. Apparent activation energies, in kilocalories per mole, also are indicated in the figures for short, medium, and long residence-time data. It is not intended that these energies should be taken as an indication of any specific physical or chemical processes but rather that they show approximate overall trends in the data. In fact, it may be noted that, almost without exception, the experimental data are fitted better by curves concave downward than by straight lines. In most cases, the apparent activation energies for the short and medium residence times are within the probable error limits of each other, and the long-residence-time energies are slightly lower, suggesting that the sulfur pickup might be governed by one process up to the neighborhood of the maximum in the pickup curve, and that other processes such as calcination and oxidation of the sulfite may be more influential in determining the temperature dependence during the later stages of the reaction.

The apparent activation energies range from 11 to 15 kcal/mole for No. 1683 and the burnt limes to 24-28 kcal/mole for the other limestones and dolomites. The latter values are in agreement with the 28 kcal/mole previously reported for the reaction of No. 1359. The low values for the burnt limes are consistent with the fact that calcination is not required with these materials, so that the overall thermal requirements for the burnt limes should be lower. However, the low apparent activation energies for No. 1683 are not consistent with the values obtained for other raw stones. This may be related to the fact that No. 1683 is an aragonite rather than a calcite as are the other limestones.

It should be noted that the activation energies of raw stones indicated above are appreciably higher than those previously reported (12 to 17 kcal/mole) under Contract No. PH 86-68-84, Task 11, for a special series of high-purity limestones being screened for the full-scale TVA dry-limestone injection tests (see Appendix F). In the latter case, the size of particles examined was 20-40 microns, considerably smaller than the -140 + 200 mesh material used in the current tests. If, indeed, heat transport is an important factor in determining the overall reaction rate, it might be expected that the apparent thermal requirements would decrease as particle size is decreased since the rate of convective heat transfer per unit area increases with decreasing particle size for these small particles.

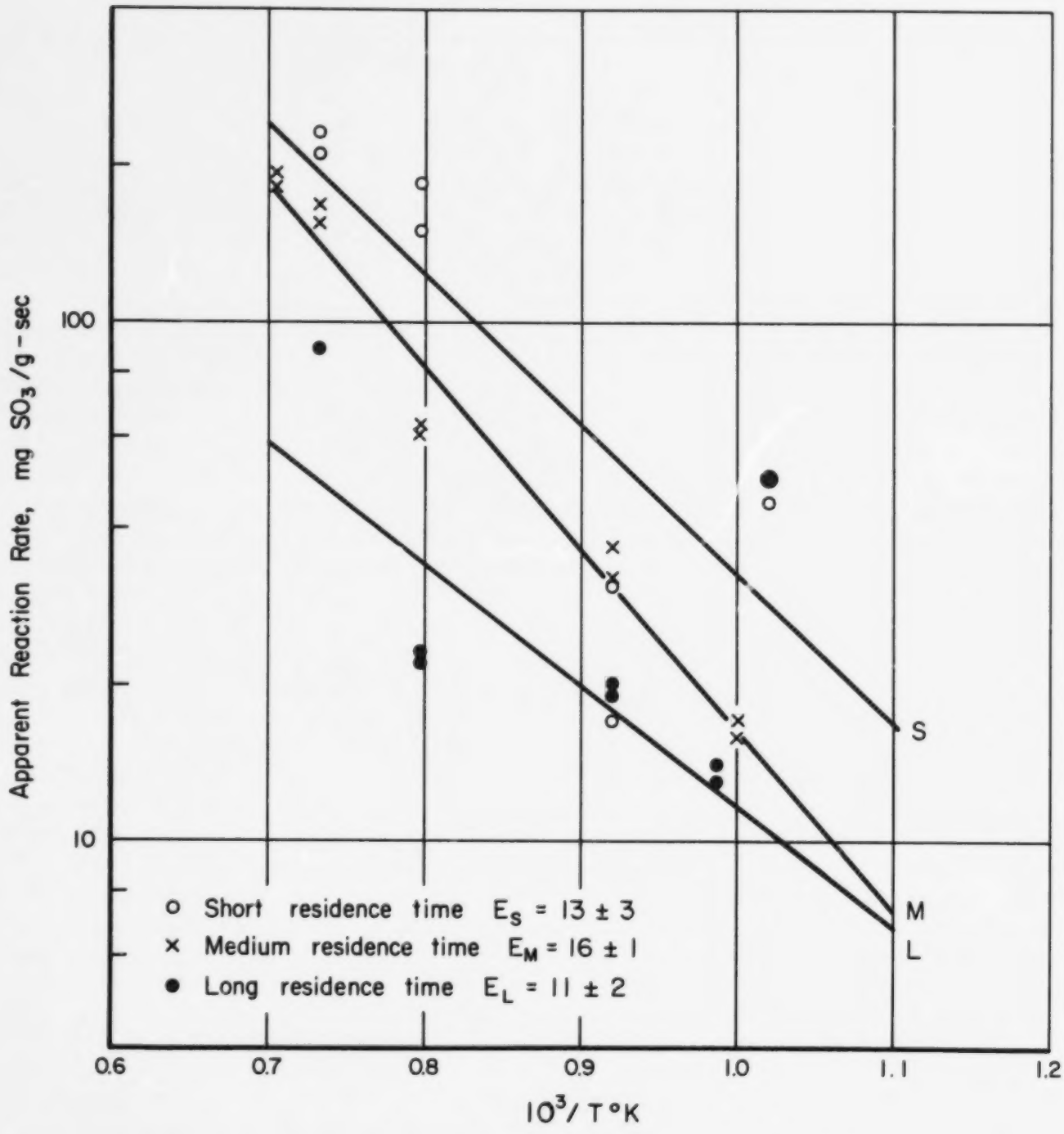

FIGURE 10. ARRHENIUS PLOT FOR NO. 1359C

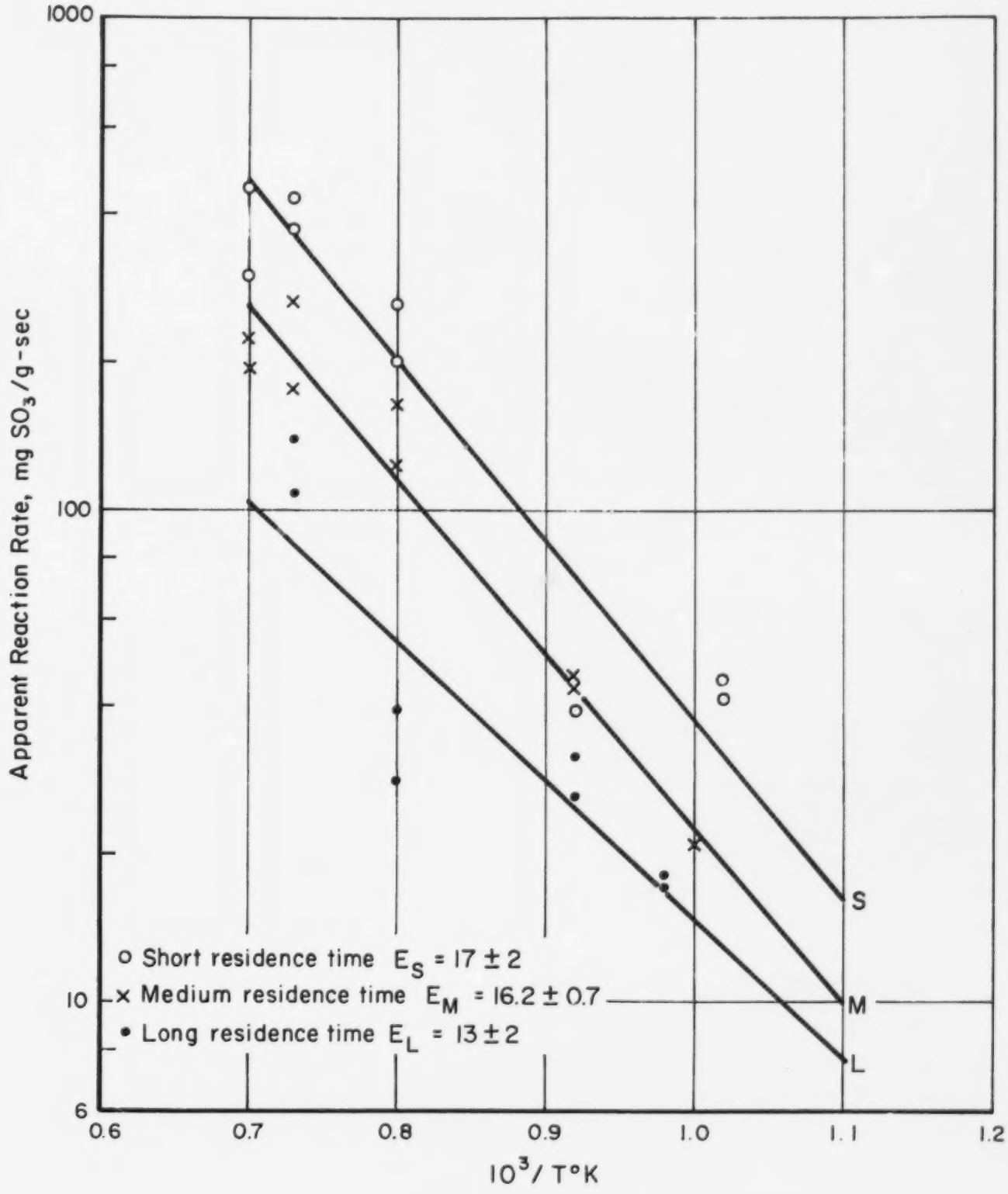

FIGURE 11. ARRHENIUS PLOT FOR NO. 1337C

Recommended Future Work

Results obtained during the current contract period have indicated that, when limestone particles are injected into a hot flue gas stream under nearly isothermal conditions, certain time factors become important. Heat-up and calcination of the particles, for example, require exposure to the hot gases for several tenths of a second. During part of this time, the temperature of the lime shell which is formed is low enough that SO_2 can be absorbed to form calcium sulfite. The sulfite can, in turn, either disproportionate or be oxidized to yield calcium sulfate. As the calcination process continues, the temperature of the lime shell rises to a point at which the calcium sulfite begins to calcine. As a result, the particles undergo a net loss in sulfur content during the later stages of calcination and heat-up. After this initial series of processes, the fully calcined particles may be expected to continue to pick up sulfur at a rate characteristic of the formation of calcium sulfate.

In a boiler, where gas temperatures drop off very rapidly between, say, 2300 and 1500°F, the heat-up and calcination problem is likely to be accentuated over that observed in nearly isothermal experiments. It is, therefore, highly important that the nature of the physical and chemical processes occurring during heat-up and calcination be thoroughly understood so that valid extrapolations from the pilot experimental work to boiler performance can be made. It is implicit that this understanding should be based upon the following factors:

(1) The rate of heat transport to and within a limestone particle

(2) The rate of mass transport to, from, and within the particle

(3) The rates of the chemical processes occurring within the particle:

  (a) Calcination
  (b) Formation and decomposition of sulfite
  (c) Formation of sulfate.

The program outlined below is suggested as a logical route for gaining insight into the above factors. It is recommended that the work be performed with a single well-defined limestone, with the purpose of developing understanding of the mechanics of the overall process.

The program would be conducted in a dispersed-phase reactor of the type used to date. However, because of the need for obtaining longer residence times and higher temperatures than are currently possible, a new dispersed-phase reactor would be required. This reactor would be approximately twice as long as the existing one, so that residence times of about 2 seconds could be achieved at 1800°F, and would be constructed of materials to permit operation up to about 2500°F. It would also be necessary to construct an appropriate calciner and preheater.

The recommended program is as follows:

(1) Conduct preliminary experiments to establish qualitatively the effect of oxygen and nitrogen oxide content of the flue gas on the reactivity of limestone with SO_2.

(2) Study the course of the reaction of raw limestone with respect to calcination, sulfite formation, and sulfate formation as a function of temperature.

(3) Study the course of the reaction of precalcined stone with SO_2 with respect to sulfite and sulfate formation. The stone would be calcined under conditions simulating those in the dispersed-phase reactor.

(4) Study the calcination rate in the reactor, using flue gas containing no sulfur.

(5) Attempt to construct a mathematical model of the reaction system in terms of gas temperature, particle composition, and time.

APPENDIX A

DISPERSED-PHASE REACTOR

APPENDIX A

DISPERSED-PHASE REACTOR

Figure A-1 is a sketch of the dispersed-phase reactor as shown in the previous Summary Report dated August 30, 1969. In the current work, the reaction section was lengthened from 60 to 72 inches to allow for more versatility in operation, and a new shell of 316 stainless steel was installed to reduce corrosion problems. Not shown in Figure A-1 are radiation screens which were placed at the top and bottom of the reaction section to reduce radiation losses and to smooth out gas flow.

Injection and collection of particles is made through the series of ports spaced every 6 inches along the reaction section. Probes for these operations are described in the body of this report and in the previous Summary Report. In operation, the mean gas temperature is determined with a multiple-shielded 10%Rh, Pt-Pt thermocouple which is inserted midway between the injection and collection probes.

Input gas-flow rates to the combustor are metered by differential flow manometers; the residence times of particles in the reactor can be determined from probe spacings and gas velocities. Reynolds numbers for the flue gas are determined from the mean temperatures and the viscosity data of Geiringer.*

The uppermost ports of the reactor are also used for withdrawal of gas samples for analysis. Probes inserted in these ports lead directly to Orsat (for CO_2 and O_2) or titration apparatus (for sulfur oxides). Techniques used in these analyses are discussed further in the text of this report.

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*P. L. Geiringer, Handbook of Heat Transfer Media, Rheinhold Publishing Corp., New York, 1962.

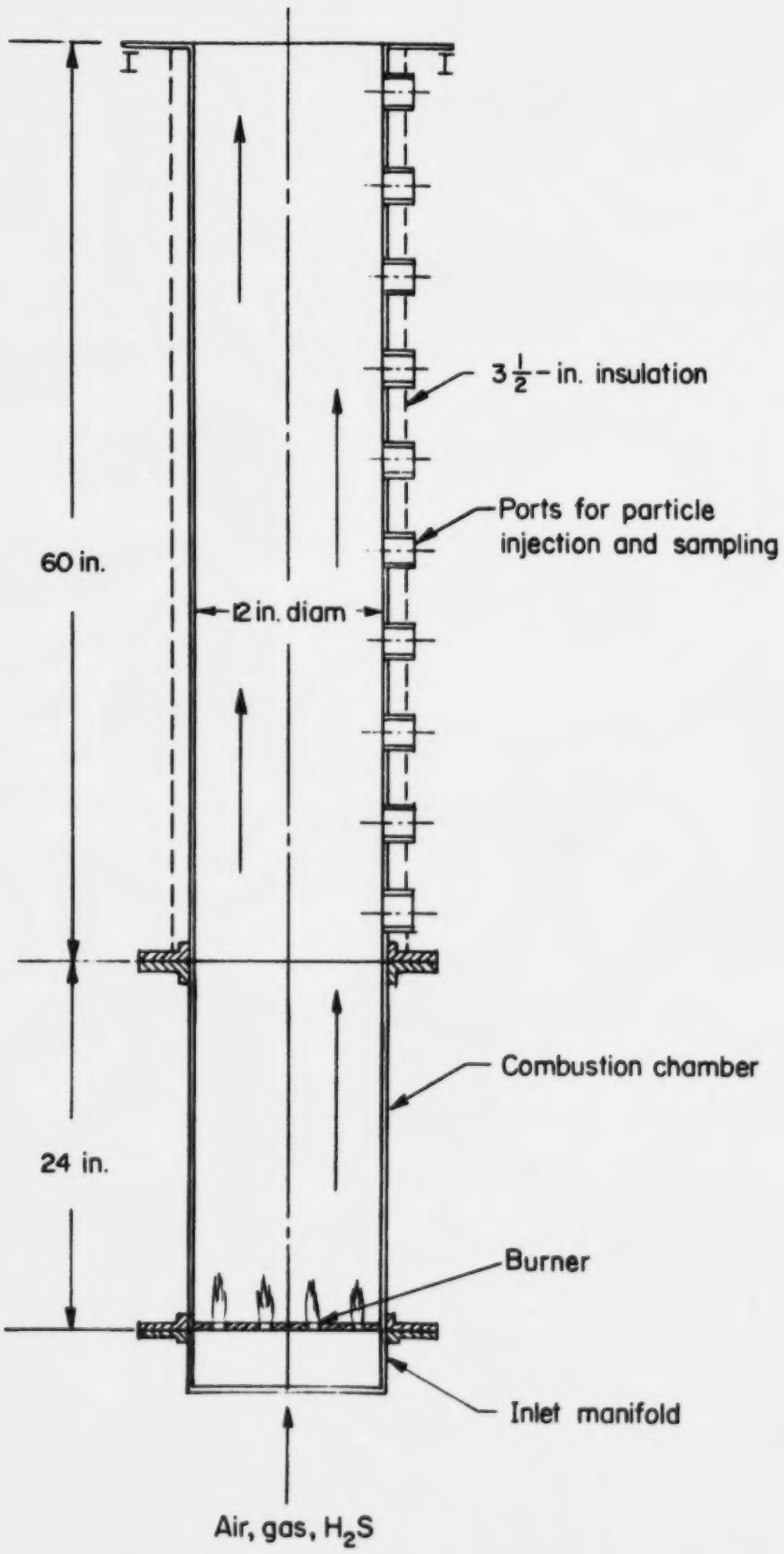

FIGURE A-1. DISPERSED-PHASE REACTOR

APPENDIX B

SPECTROCHEMICAL ANALYSIS OF STONES

TABLE B-1. SPECTROCHEMICAL ANALYSIS OF STONES(a)

Results Reported as Percentage by Weight of Ignited Sample (900 C)

Stone Number(b)	Loss on Ignition (900°C)	Component									
		SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	TiO_2	SrO	Na_2O	K_2O	MnO_2
1337 AR	47.5	0.78	0.15	0.25	45.0	53	0.02	<0.03	<0.02	<0.1	<0.03
1337 B	47.5	0.77	0.13	0.24	43.5	54	<0.02	<0.03	<0.02	<0.1	<0.03
1337 C	47.3	0.92	0.15	0.33	44.0	54	<0.03	<0.03	<0.02	<0.1	<0.03
1337 F	47.3	0.86	0.15	0.25	42.5	56	<0.03	<0.03	<0.02	<0.1	<0.03
1337 M	47.3	0.78	0.14	0.36	43.0	55	<0.03	<0.03	<0.02	<0.1	<0.03
1359 AR	43.6	0.85	0.30	0.17	1.07	97	<0.05	0.07	<0.02	<0.1	<0.05
1359 B	43.6	1.13	0.27	0.23	1.11	97	<0.05	0.08	<0.02	<0.1	<0.05
1359 F	43.6	0.90	0.30	0.20	1.10	97	<0.05	0.07	<0.02	<0.1	<0.05
1359 10/28M	43.6	1.07	0.29	0.22	1.16	97	<0.05	0.07	<0.02	<0.1	<0.05
1360 AR	43.7	4.08	0.29	2.04	14.6	78	0.05	0.05	0.06	<0.1	0.25
1360 B	43.7	3.85	0.32	1.83	13.4	80	<0.05	<0.05	0.05	<0.1	0.21
1360 C	43.1	5.20	0.40	1.67	13.3	79	<0.05	0.05	0.07	<0.1	0.17
1360 F	44.2	2.74	0.35	1.84	18.5	76	<0.05	0.05	0.06	<0.1	0.21
1360 10/28M	44.5	3.65	0.27	1.25	13.0	81	<0.05	0.05	0.05	<0.1	0.16
1373 B	41.8	4.20	0.95	1.06	5.30	85	0.07		0.07	0.20	0.33
1373 1 Qt. FR	41.9	3.75	1.02	1.23	6.0	87	0.07		0.12	0.22	0.37
1384 B	43.6	<1.0	<0.3	<0.2	0.93	97	<0.03		0.06	<0.1	<0.03
1384 C	44.0	<1.0	<0.3	<0.2	0.99	97	0.04		0.03	<0.1	<0.03
1384 F	43.8	1.2	<0.3	0.36	1.24	96	0.04		0.03	<0.1	<0.03
1384 M	43.8	1.2	<0.3	<0.3	1.24	96	0.04		0.03	<0.1	<0.03
1683 B	44.2	1.10	<0.3	<0.2	0.80	Bal.	<0.05		0.44	<0.1	<0.05
1683 C	44.3	1.40	<0.20	0.42	2.36	94	<0.03		0.48	<0.10	0.06
1683 F	44.3	1.76	<0.20	0.11	0.83	96	<0.03		0.28	<0.10	<0.03
1683 M	43.7	4.09	<0.20	0.23	2.23	92	<0.03		0.53	<0.10	<0.03
1683 1 Qt. FR	44.5	1.00	<0.3	<0.2	0.82	Bal.	<0.05		0.40	<0.1	<0.05

(a) Supplied by Bituminous Coal Research, Inc.

(b) B = bulk, AR = as received, M = medium, F = fine, C = coarse.

APPENDIX C

REACTOR DATA

TABLE C-1. REACTOR DATA

Run Number	Stone Number[a]	Injection Data: Time, min	Injection Data: Rate, g/min	Gas Temp, °F	Reynolds Number	Residence Time, sec	Product Analysis[b]: Ca	Mg	$SO_4^=$	Percent CaO Utilization	SO_3, mg per gram calcine	Calculated Percent Calcination	Gas Analysis, volume percent[c]: SO_2	SO_3	CO_2	O_2
2-6-L	1359H	1	0.9	1500	1700	0.36	53.3	0.5	9.0	3.9	54	71	0.300	0.0049	10.0	3.0
2-6-M	1359H	1.5	1.0	1500	1700	0.36	52.8	0.5	9.6	4.2	59	70	0.300	0.0049	10.0	3.0
2-5-V	1359H	3.5	1.7	1504	1700	1.14	55.8	0.6	12.9	5.4	75	82	0.300	0.0049	10.0	3.0
2-5-W	1359H	3	1.4	1504	1700	1.14	55.7	0.6	12.6	5.3	73	82	0.300	0.0049	10.0	3.0
2-4-X	1359H	2.5	1.7	1508	1700	1.7	59.4	0.7	13.5	5.3	73	92	0.303	0.0053	10.2	2.6
2-4-Y	1359H	3	1.5	1508	1700	1.7	57.6	0.7	13.9	5.6	78	88	0.303	0.0053	10.2	2.6
11-4-J	1359H	1.5	0.73	1800	2700	0.18	61.3	0.4	14.2	5.4	75	97	0.304	0.0028	10.2	2.8
11-4-K	1359H	2	0.9	1800	2700	0.18	63.8	0.4	11.1	4.0	56	99	0.304	0.0028	10.2	2.8
10-24-A	1359H	3	0.23	1802	2700	0.58	46.9	0.8	13.4	6.6	92	55	0.303	0.0035	10.2	2.8
10-24-B	1359H	3	0.50	1802	2700	0.58	53.5	0.7	11.3	4.9	68	74	0.303	0.0035	10.2	2.8
1-14-A	1359H	4	0.08	1791	1800	0.65	63.2	0.4	14.0	5.2	71	101	0.303	0.003	10.5	3.1
1-14-B	1359H	5	1.1	1791	1800	0.65	60.4	0.5	15.9	6.1	85	97	0.303	0.003	10.5	3.1
11-6-C	1359H	1.5	1.8	2006	3500	0.12	44.4	0.7	6.6	3.2 ± 0.8[d]	44 ± 12	--	0.300	0.0028	10.0	2.5
11-6-D	1359H	1.5	1.6	2006	3500	0.12	47.9	0.7	5.7	2.7 ± 0.7[d]	37 ± 12	--	0.300	0.0028	10.0	2.5
10-28-G	1359H	1.5	1.53	1996	3400	0.40	57.1	0.6	15.7	6.4	89	89	0.295	0.0029	10.8	2.6
10-28-H	1359H	3	0.53	1996	3400	0.40	55.3	0.4	17.4	7.3	101	86	0.295	0.0029	10.8	2.6
1-6-E	1359H	3	0.95	2000	3300	0.61	63.1	0.8	13.0	4.8	66	100	0.302	0.0033	10.9	2.7
1-6-F	1359H	3	1.0	2000	3300	0.61	62.4	0.7	11.4	4.2	58	97	0.302	0.0033	10.9	2.7
11-7-N	1359H	2	1.3	2100	3900	0.10	75.1	0.3	9.0	4.4 ± 1.2[d]	61 ± 16	--	0.298	0.0023	11.0	2.6
11-7-O	1359H	4	1.4	2100	3900	0.10	47.9	0.4	9.8	4.8	66	54	0.298	0.0023	11.0	2.6
11-13-A	1359H	3	1.3	2102	3600	0.36	49.1	0.8	14.0	6.6	92	64	0.300	0.0028	10.2	2.8
11-13-B	1359H	3	1.65	2102	3600	0.36	79.0	0.4	14.3	7.2 ± 1.8[d]	99 ± 25	--	0.300	0.0028	10.2	2.8
11-19-N	1359H	4	0.9	2100	3800	0.50	55.4	0.6	11.7	4.9	68	80	0.302	0.0026	10.2	2.6
11-19-O	1359H	4	1.8	2100	3800	0.50	53.7	0.4	12.4	5.4	74	76	0.302	0.0026	10.2	2.6
2-12-E	1359C	2	0.55	1305	1600	0.44	67.7	0.9	4.6	1.6	22	101	0.300	0.0005	10.0	3.0
2-12-F	1359C	2	0.9	1305	1600	0.44	67.7	0.9	4.1	1.4	20	101	0.300	0.0005	10.0	3.0
2-12-G	1359C	5	0.7	1339	1600	1.39	67.7	0.9	4.7	1.6	22	101	0.300	0.0005	10.0	3.0
2-12-H	1359C	5	0.8	1339	1600	1.39	67.7	0.9	4.8	1.6	23	101	0.300	0.0005	10.0	3.0
2-12-R	1359C	4	1.5	1372	1600	2.1	64.9	0.8	5.8	2.1	29	97	0.300	0.0005	10.0	3.0
2-12-S	1359C	5	1.7	1372	1600	2.1	64.9	0.9	0.7	5.6	29	96	0.300	0.0005	10.0	3.0

TABLE C-1. (Continued)

Run Number	Stone Number[a]	Injection Data: Time, min	Injection Data: Rate, g/min	Gas Temp, °F	Reynolds Number	Residence Time, sec	Product Analysis[b]: Ca	Product Analysis[b]: Mg	Product Analysis[b]: $SO_4^=$	Percent CaO Utilization	SO_3, mg per gram calcine	Calculated Percent Calcination	Gas Analysis, volume percent[c]: SO_2	Gas Analysis, volume percent[c]: SO_3	Gas Analysis, volume percent[c]: CO_2	Gas Analysis, volume percent[c]: O_2
2-6-P	1359C	1	1.5	1500	1700	0.36	69.6	0.4	1.4	0.5	6	101	0.300	0.0049	10.0	3.0
2-6-Q	1359C	1	1.5	1500	1700	0.36	68.5	0.4	2.3	0.8	11	100	0.300	0.0049	10.0	3.0
2-5-R	1359C	3.5	1.2	1504	1700	1.14	61.6	0.6	8.0	3.0	42	92	0.300	0.0049	10.0	3.0
2-5-S	1359C	4	1.1	1504	1700	1.14	62.2	0.6	6.7	2.5	35	92	0.300	0.0049	10.0	3.0
2-4-R	1359C	2.5	2.1	1506	1700	1.7	66.8	0.7	6.7	2.3	32	101	0.303	0.0053	10.2	2.6
2-4-S	1359C	2.5	2.1	1506	1700	1.7	66.5	0.7	6.6	2.3	32	101	0.303	0.0053	10.2	2.6
2-6-E	1359C	5	1.0	1500	1700	1.72	64.6	0.6	6.9	2.5	34	97	0.300	0.0049	10.0	3.0
2-6-F	1359C	5	1.0	1500	1700	1.72	62.5	0.6	6.3	2.3	32	92	0.300	0.0049	10.0	3.0
11-4-P	1359C	2	?	1800	2700	0.18	66.6	0.6	6.8	2.4	33	101	0.304	0.0028	10.2	2.8
11-4-Q	1359C	2	1.6	1800	2700	0.18	64.7	0.7	5.4	1.9	27	96	0.304	0.0028	10.2	2.8
10-23-J	1359C	3	1.20	1800	2700	0.58	59.5	0.8	6.5	2.5	35	85	0.300	0.0029	10.4	2.9
10-23-K	1359C	3	0.50	1800	2700	0.58	56.7	0.7	6.4	2.6	36	78	0.300	0.0029	10.4	2.9
1-28-J	1359C	3	2.2	1803	2500	0.95	70.5	0.7	4.7	1.6	21	106	0.303	0.0038	10.6	2.4
1-28-K	1359C	3	1.1	1803	2500	0.95	69.3	1.1	4.8	1.6	22	104	0.303	0.0038	10.6	2.4
11-6-J	1359C	2	1.1	2006	3500	0.12	60.9	0.7	5.3	2.0	28	87	0.300	0.0028	10.0	2.5
11-6-K	1359C	2	0.8	2006	3500	0.12	62	0.7	4.9	1.8	25	89	0.300	0.0028	10.0	2.5
10-28-A	1359C	3	0.80	1996	3400	0.40	57.1	0.6	10.9	4.4	62	84	0.295	0.0029	10.8	2.6
10-28-B	1359C	3	0.65	1996	3400	0.40	55.0	0.5	11.5	4.9	67	79	0.295	0.0029	10.8	2.6
1-6-G	1359C	3	2.5	2000	3300	0.61	60.0	0.8	10.0	3.9	54	90	0.302	0.0033	10.9	2.7
1-6-H	1359C	3	N.S.	2000	3300	0.61	--	--	--	--	--	--	0.302	0.0033	10.9	2.7
10-30-C	1359C	3	0.6	2100	3800	0.34	65.2	0.5	13.4	4.8	66	104	0.299	0.0029	10.0	3.0
10-30-D	1359C	3	0.8	2100	3800	0.34	65.8	0.6	12.8	4.5	63	105	0.299	0.0029	10.0	3.0
1-23-N	1359	1	2.8	2006	3600	0.11	43.5	0.6	5.9	3.2	44	31	0.652	0.004	10.6	2.8
1-23-O	1359	1	2.4	2006	3600	0.11	43.0	0.6	6.1	3.3	46	28	0.652	0.004	10.6	2.8
12-20-G	1359	1	1.0	2001	3400	0.12	42.4	0.4	5.4	3.0	41	25	0.033	0.007	10.3	2.9
12-20-H	1359	2	1.2	2001	3400	0.12	42.6	0.4	5.7	3.1	43	26	0.033	0.007	10.3	2.9
12-3-E	1359	2	1.3	2000	3300	0.13	40.4	0.5	6.2	3.6	49	16	0.583	0.0033	10.4	2.7
12-3-F	1359	1.5	1.3	2000	3300	0.13	37.8	0.3	5.8	3.6	49	0	0.583	0.0033	10.4	2.7
1-23-C	1359	1	3.0	2006	3700	0.12	45.9	0.4	2.8	1.4	20	37	0.026	0.0009	10.6	2.8
1-23-D	1359	1.3	1.9	2006	3700	0.12	45.0	0.4	2.0	10.0	14	32	0.026	0.0009	10.6	2.8

TABLE C-1. (Continued)

Run Number	Stone Number[a]	Injection Data: Time, min	Injection Data: Rate, g/min	Gas Temp, °F	Reynolds Number	Residence Time, sec	Product Analysis[b]: Ca	Product Analysis[b]: Mg	Product Analysis[b]: $SO_4^=$	Percent CaO Utilization	SO_3, mg per gram calcine	Calculated Percent Calcination	Gas Analysis, volume percent[c]: SO_2	Gas Analysis, volume percent[c]: SO_3	Gas Analysis, volume percent[c]: CO_2	Gas Analysis, volume percent[c]: O_2
1-23-E	1359	1	2.3	2006	3600	0.12	45.8	0.4	~0	--	--	--	0.0073	Not	10.6	2.8
1-23-F	1359	1	2.7	2006	3600	0.12	45.8	0.4	~0	--	--	--	0.0073	meas.	10.6	2.8
1-9-R	1359	1.5	2.9	2000	3300	0.13	42.1	0.5	6.5	3.6	50	25	0.077	0.0015	9.9	2.8
1-9-S	1359	1.5	2.7	2000	3300	0.13	41.3	0.4	5.1	2.9	40	19	0.077	0.0015	9.9	2.8
1-9-T	1359	1.5	2.1	2000	3300	0.13	42.1	0.4	5.8	3.2	44	24	0.18	0.0028	9.9	2.8
1-9-U	1359	2	2.0	2000	3300	0.13	40.3	0.4	5.5	3.2	44	14	0.18	0.0028	9.9	2.8
2-6-GG	Basic	1	1.2	1500	1720	0.36	20.6	12.4	~0	--	--	--	0.300	0.0049	10.0	3.0
2-6-HH	Basic	1	1.2	1500	1720	0.36	20.5	12.4	~0	--	--	--	0.300	0.0049	10.0	3.0
2-5-G	Basic	2.5	2.2	1504	1700	1.14	21.6	13.1	6.1	4.2 ± 8[d]	37 ± 7	--	0.300	0.0049	10.0	3.0
2-5-H	Basic	3	2.2	1504	1700	1.14	21.5	13.2	5.5	3.7 ± 0.7[d]	33 ± 6	--	0.300	0.0049	10.0	3.0
2-4-A	Basic	3	?	1506	1700	1.7	24.3	14.9	10.7	7.5 ± 1.3[d]	65 ± 11	--	0.303	0.0053	10.2	2.6
2-4-B	Basic	3	2.0	1506	1700	1.7	25.4	15.3	12.3	8.7 ± 1.5[d]	76 ± 13	--	0.303	0.0053	10.2	2.6
2-6-A	Basic	2.5	3.2	1500	1700	1.72	26.1	14.8	6.8	4.3 ± 0.8[d]	37 ± 7	--	0.300	0.0049	10.0	3.0
2-6-B	Basic	2.5	3.2	1500	1700	1.72	26.0	15.1	6.2	4.2 ± 0.8[d]	37 ± 7	--	0.300	0.0049	10.0	3.0
11-4-C	Basic	1.5	1.3	1800	2700	0.18	24.6	14.7	12.3	11.6	101	-30	0.304	0.0028	10.2	2.8
11-4-D	Basic	1.5	1.6	1800	2700	0.18	24.9	14.8	9.0	8.4	73	-34	0.304	0.0028	10.2	2.8
10-24-C	Basic	3	0 50	1802	2700	0.58	27.0	24.3	24.3	20.9	182	27	0.303	0.0035	10.2	2.8
10-24-D	Basic	3	1.40	1802	2700	0.58	29.1	19.4	21.9	17.5	153	42	0.303	0.0035	10.2	2.8
1-28-C	Basic	2	2.8	1803	2500	0.95	32.9	19.8	20.6	14.6	127	71	0.303	0.0038	10.6	2.4
1-28-D	Basic	3	2.0	1803	2500	0.95	32.1	19.6	25.9	18.8	164	75	0.303	0.0038	10.6	2.4
10-4-C	Basic	3	1.16	1902	3200	0.46	31.0	18.3	20.9	15.7	137	57	0.300	0.0032	10.0	2.8
10-4-D	Basic	3	1.05	1902	3200	0.46	NS	NS	17.4	12.7 ± 2.1[d]	110 ± 18	--	0.300	0.0032	10.0	2.8
10-4-E	Basic	3	1.10	1902	3200	0.46	NS	NS	20.5	15.2 ± 2.5[d]	132 ± 22	--	0.300	0.0032	10.0	2.8
1-13-A	Basic[h]	2	1.3	1903	2900	0.51	33.8	20.4	18.6	12.8	112	73	0.296	0.0036	10.6	2.7
1-13-B	Basic[h]	2	1.0	1903	2900	0.51	33.4	20.0	19.8	13.8	120	73	0.296	0.0036	10.6	2.7
1-13-J	Basic[i]	4	0.22	1903	2900	0.51	31.9	20.4	26.1	19.0	166	74	0.296	0.0036	10.6	2.7
1-13-K	Basic[i]	4	0.45	1903	2900	0.51	32.8	19.8	24.1	17.1	149	76	0.296	0.0036	10.6	2.7
10-18-G	Basic[g]	3	0.60	1900	3100	0.47	31.3	19.3	27.9	20.7	181	73	0.297	0.0027	10.2	2.8
10-18-H	Basic[g]	4	0.60	1900	3100	0.47	31.7	19.4	26.2	19.2	167	73	0.297	0.0027	10.2	2.8
10-10-A	Basic[f]	4	1.10	1903	3100	0.47	31.0	17.1	15.5	11.6	101	46	0.303	0.0028	10.2	2.8
10-10-B	Basic[f]	4	1.40	1903	3100	0.47	33.3	19.2	16.3	11.4	99	66	0.303	0.0028	10.2	2.8

TABLE C-1. (Continued)

Run Number	Stone Number[a]	Injection Data: Time, min	Injection Data: Rate, g/min	Gas Temp, °F	Reynolds Number	Residence Time, sec	Product Analysis[b]: Ca	Product Analysis[b]: Mg	Product Analysis[b]: $SO_4^=$	Percent CaO Utilization	SO_3, mg per gram calcine	Calculated Percent Calcination	Gas Analysis, volume percent[c]: SO_2	Gas Analysis, volume percent[c]: SO_3	Gas Analysis, volume percent[c]: CO_2	Gas Analysis, volume percent[c]: O_2
1-13-R	Basic[j]	2	2	1903	2900	0.51	30.3	17.7	27.0	20.7	180	63	0.293	0.0032	10.2	3.0
1-13-S	Basic[j]	2	2	1903	2900	0.51	31.5	18.3	20.7	15.3	133	60	0.293	0.0032	10.2	3.0
12-20-E	Basic	1	2.5	2001	3400	0.12	29.4	16.9	8.4	6.6	58	17	0.033	0.007	10.3	2.9
12-20-F	Basic	1	1.9	2001	3400	0.12	29.9	17.2	9.4	7.3	64	24	0.033	0.007	10.3	2.9
12-20-C	Basic	1	2.9	2001	3400	0.12	28.0	15.9	8.6	7.1	62	3	0.083	0.0016	10.3	2.9
12-20-D	Basic	1	2.5	2001	3400	0.12	27.2	15.8	8.5	7.3	63	-6	0.083	0.0016	10.3	2.9
12-20-A	Basic	1.5	2.6	2001	3400	0.12	27.6	16.4	12.0	10.1	88	6	0.128	0.0020	10.3	2.9
12-20-B	Basic	1	2.6	2001	3400	0.12	27.3	15.8	9.3	7.9	69	-3	0.128	0.0020	10.3	2.9
12-3-G	Basic	1.25	1.3	2000	3300	0.13	26.1	15.5	10.6	9.4	82	-15	0.198	0.0020	10.4	2.7
12-3-H	Basic	1	1.5	2000	3300	0.13	24.4	14.7	6.8	6.5	56	-47	0.198	0.0020	10.4	2.7
12-3-A	Basic	2	1.5	2000	3300	0.13	25.6	14.6	11.2	10.2	89	-20	0.289	0.0025	10.4	2.7
12-3-B	Basic	2	1.25	2000	3300	0.13	25.8	15.9	9.8	8.8	77	-20	0.289	0.0025	10.4	2.7
12-3-C	Basic	1	1.5	2000	3300	0.13	25.1	14.8	9.1	8.4	73	-30	0.583	0.0033	10.4	2.7
12-3-D	Basic	1	1.2	2000	3300	0.13	25.5	15.2	11.4	10.4	91	-20	0.583	0.0033	10.4	2.7
1-23-G	Basic	1	2.8	2006	3600	0.12	31.3	18.0	--	--	--	--	0.0073	Not	10.6	2.8
1-23-H	Basic	1	2.9	2006	3600	0.12	31.6	18.2	--	--	--	--	0.0073	meas.	10.6	2.8
1-23-J	Basic	1	3.0	2006	3600	0.12	30.5	17.5	10.8	7.6	66	31	0.1375	0.0023	10.6	2.8
1-23-K	Basic	1	2.7	2006	3600	0.12	28.2	15.9	6.8	5.6	49	1	0.1375	0.0023	10.6	2.8
1-23-L	Basic	1	4.6	2006	3600	0.11	26.1	15.3	8.0	7.1	62	-21	0.652	0.004	10.6	2.8
1-23-M	Basic	1	3.0	2006	3600	0.11	26.9	15.3	9.4	8.1	71	-8	0.652	0.004	10.6	2.8
1-23-A	Basic	2	2.5	2006	3700	0.12	27.9	16.4	5.0	4.2	36	-6	0.026	0.0009	10.6	2.8
1-23-B	Basic	1	2.7	2006	3700	0.12	27.9	16.2	5.4	4.5	39	-5	0.026	0.0009	10.6	2.8
1-9-V	Basic	1.5	2.2	2000	3300	0.13	25.7	16.3	10.1	9.1	80	-21	0.18	0.0028	9.9	2.8
1-9-W	Basic	1.5	1.6	2000	3300	0.13	25.5	16.1	10.3	9.4	82	-23	0.18	0.0028	9.9	2.8
1-9-P	Basic	1	4	2000	3300	0.13	28.6	17.6	12.4	10.1	88	17	0.077	0.0015	9.9	2.8
1-9-Q	Basic	2	1.5	2000	3300	0.13	27.8	17.5	12.3	10.3	90	9	0.077	0.0015	9.9	2.8
11-7-C	Basic	2	1.2	2100	3900	0.10	23.0	17.0	19.9	15.8[e]	138	39	0.298	0.0023	11.0	2.6
11-7-D	Basic	2	1.5	2100	3900	0.10	25.1	12.2	16.1	12.7[e]	111	34	0.298	0.0023	11.0	2.6
10-30-P	Basic	3	1.1	2100	3800	0.34	32.3	18.0	24.0	17.3	151	73	0.299	0.0029	10.0	3.0
10-30-Q	Basic	3	0.95	2100	3800	0.34	32.5	18.4	29.1	20.8	181	84	0.299	0.0029	10.0	3.0

TABLE C-1. (Continued)

Run Number	Stone Number[a]	Injection Data: Time, min	Injection Data: Rate, g/min	Gas Temp, °F	Reynolds Number	Residence Time, sec	Product Analysis[b]: Ca	Product Analysis[b]: Mg	Product Analysis[b]: $SO_4^=$	Percent CaO Utilization	SO_3, mg per gram calcine	Calculated Percent Calcination	Gas Analysis, volume percent[c]: SO_2	Gas Analysis, volume percent[c]: SO_3	Gas Analysis, volume percent[c]: CO_2	Gas Analysis, volume percent[c]: O_2
11-19-E	Basic	3	1.7	2100	3800	0.50	30.7	19.6	22.3	16.9	147	57	0.302	0.0026	10.2	2.6
11-19-F	Basic	3	1.9	2100	3800	0.50	42.8	18.8	21.6	16.1 ± 2.6[d]	140 ± 23	--	0.302	0.0026	10.2	2.6
10-18-C	1683[f]	3	1.60	1900	3100	0.47	54.3	0.4	11.2	4.8	64	81	0.297	0.0027	10.2	2.8
10-18-D	1683[f]	3	0.60	1900	3100	0.47	52.9	0.3	8.9	3.9	53	74	0.297	0.0027	10.2	2.8
10-18-L	1683[g]	4	1.05	1900	3100	0.47	54.1	0.5	16.9	7.3	98	87	0.297	0.0027	10.2	2.8
10-18-M	1683[g]	4	0.87	1900	3100	0.47	NS	NS	23.6	12.7 ± 3[d]	171 ± 41	--	0.297	0.0027	10.2	2.8
1-13-X	1683[j]	2	1.5	1903	2900	0.51	51.0	2.1	25.5	11.6	156	88	0.293	0.0032	10.2	3.0
1-13-Y	1683[j]	2	2.3	1903	2900	0.51	53.2	1.1	23.7	10.4	139	92	0.293	0.0032	10.2	3.0
1-13-C	1683[h]	1.5	2.8	1903	2900	0.51	59.2	0.5	12.3	4.8	64	94	0.296	0.0036	10.6	2.7
1-13-D	1683[h]	1.5	0.9	1903	2900	0.51	58.5	0.5	15.7	6.2	83	96	0.296	0.0036	10.6	2.7
1-13-L	1683[i]	4	0.35	1903	2900	0.51	52.6	0.6	21.1	9.3	125	87	0.296	0.0036	10.6	2.7
1-13-M	1683[i]	1	2	1903	2900	0.51	51.7	0.6	15.9	7.2	96	78	0.296	0.0036	10.6	2.7
2-6-X	1683	1	2	1500	1700	0.36	38.5	0.3	3.6	2.2	29	5	0.300	0.0049	10.0	3.0
2-6-Y	1683	1	1.5	1500	1700	0.36	37.7	0.3	3.7	2.3	31	0	0.300	0.0049	10.0	3.0
2-5-C	1683	2.5	2.9	1504	1700	1.14	40.4	0.4	6.3	3.6	49	20	0.300	0.0049	10.0	3.0
2-5-D	1683	2	2.3	1504	1700	1.14	40.4	0.4	7.4	4.3	57	21	0.300	0.0049	10.0	3.0
2-4-E	1683	3	2.6	1506	1700	1.7	45.2	0.4	9.8	5.0	68	48	0.303	0.0053	10.2	2.6
2-4-F	1683	2.5	2.5	1506	1700	1.7	45.4	0.4	9.9	5.1	68	48	0.303	0.0053	10.2	2.6
11-1-E	1683	1	2.5	1800	2600	0.19	42.9	0.5	5.9	3.2	43	32	0.301	0.0026	11.0	2.5
11-1-F	1683	1	1.4	1800	2600	0.19	40.7	0.4	7.4	4.2	57	23	0.301	0.0026	11.0	2.5
10-24-L	1683	3	1.00	1802	2700	0.58	43.2	0.5	18.6	10.0	134	51	0.303	0.0035	10.2	2.8
10-24-M	1683	3	0.40	1802	2700	0.58	44.4	0.5	20.4	10.7	143	59	0.303	0.0035	10.2	2.8
1-28-R	1683	1.5	4.0	1803	2500	0.95	58.6	0.5	11.4	4.5	61	92	0.303	0.0038	10.6	2.4
1-28-S	1683	1.5	2.1	1803	2500	0.95	57.3	0.5	13.7	5.6	75	91	0.303	0.0038	10.6	2.4
10-18-E	1683	3	1.80	1900	3100	0.47	57.1	0.4	14.1	5.7	77	91	0.297	0.0027	10.2	2.8
10-18-F	1683	3	1.60	1900	3100	0.47	57.0	0.3	14.4	5.9	79	91	0.297	0.0027	10.2	2.8
11-7-E	1683	2	1.7	2100	3900	0.10	53.5	0.3	4.1	2.0 ± 0.5[d]	27 ± 7	--	0.298	0.0023	11.0	2.6
11-7-F	1683	2	1.95	2100	3900	0.10	42.0	0.3	5.0	2.8	37	26	0.298	0.0023	11.0	2.6
10-30-L	1683	3	1.0	2100	3800	0.34	53.5	0.5	15.3	6.7	89	83	0.299	0.0029	10.0	3.0
10-30-M	1683	3	0.8	2100	3800	0.34	44.5	0.4	15.4	8.0	108	52	0.299	0.0029	10.0	3.0

BATTELLE MEMORIAL INSTITUTE – COLUMBUS LABORATORIES

TABLE C-1. (Continued)

Run Number	Stone Number[a]	Injection Data: Time, min	Injection Data: Rate, g/min	Gas Temp, °F	Reynolds Number	Residence Time, sec	Product Analysis[b]: Ca	Product Analysis[b]: Mg	Product Analysis[b]: $SO_4^=$	Percent CaO Utilization	SO_3, mg per gram calcine	Calculated Percent Calcination	Gas Analysis, volume percent[c]: SO_2	Gas Analysis, volume percent[c]: SO_3	Gas Analysis, volume percent[c]: CO_2	Gas Analysis, volume percent[c]: O_2
11-19-A	1683	3	1.7	2100	3800	0.50	53.0	0.4	13.4	5.9	79	79	0.302	0.0026	10.2	2.6
11-19-B	1683	3	1.2	2100	3800	0.50	79.4	0.5	13.8	7.0 ± 1.8[d]	95 ± 24	--	0.302	0.0026	10.2	2.6
2-6-AA	1384	1	1.5	1500	1720	0.36	38.6	0.3	~0	--	--	--	0.300	0.0049	10.0	3.0
2-6-BB	1384	1	1	1500	1720	0.36	38.8	0.3	~0	--	--	--	0.300	0.0049	10.0	3.0
2-5-A	1384	3	2.0	1504	1700	1.14	39.8	0.5	5.6	3.3	45	11	0.300	0.0049	10.0	3.0
2-5-B	1384	2.5	2.4	1504	1700	1.14	39.4	0.5	5.0	3.0	41	8	0.300	0.0049	10.0	3.0
2-4-G	1384	2.5	2.0	1506	1700	1.7	44.1	0.5	8.8	4.6	64	37	0.303	0.0053	10.2	2.6
2-4-H	1384	3	1.9	1506	1700	1.7	44.1	0.5	8.0	4.2	58	36	0.303	0.0053	10.2	2.6
11-4-G	1384	1.5	?	1800	2700	0.18	40.1	0.6	7.1	4.1	57	15	0.304	0.0028	10.2	2.8
11-4-H	1384	1.5	0.8	1800	2700	0.18	40.0	0.6	8.1	4.7	65	16	0.304	0.0028	10.2	2.8
10-24-G	1384	3	0.50	1802	2700	0.58	42.6	0.7	21.8	11.9	165	49	0.303	0.0035	10.2	2.8
10-24-H	1384	3	1.00	1802	2700	0.58	43.6	0.6	22.6	12.1	167	79	0.303	0.0035	10.2	2.8
1-28-N	1384	2	3.5	1803	2500	0.95	54.9	0.5	16.2	6.9	95	84	0.303	0.0038	10.6	2.4
1-28-O	1384	2	3.3	1803	2500	0.95	54.3	0.5	14.1	6.0	84	80	0.303	0.0038	10.6	2.4
11-7-G	1384	2	1.4	2100	3900	0.10	33.8	0.4	7.8	3.7 ± 1.0[d]	52 ± 14	--	0.298	0.0023	11.0	2.6
11-7-H	1384	2	1.15	2100	3900	0.10	36.9	0.3	7.0	3.4 ± 0.9[d]	47 ± 12	--	0.298	0.0023	11.0	2.6
10-30-J	1384	3	1.2	2100	3800	0.34	55.7	0.5	21.4	8.9	124	92	0.299	0.0029	10.0	3.0
10-30-K	1384	3	1.1	2100	3800	0.34	53.7	0.5	21.4	9.3	128	86	0.299	0.0029	10.0	3.0
11-19-G	1384	4	1.4	2100	3800	0.50	50.5	0.7	16.2	7.5	103	71	0.302	0.0026	10.2	2.6
11-19-H	1384	4	1.4	2100	3800	0.50	78.4	0.5	14.5	7.3 ± 1.8[d]	100 ± 25	--	0.302	0.0026	10.2	2.6
2-6-EE	TVA	1	2.8	1500	1720	0.36	36.8	0.7	~0	--	--	--	0.300	0.0049	10.0	3.0
2-6-FF	TVA	1	1	1500	1720	0.36	36.1	0.7	~0	--	--	--	0.300	0.0049	10.0	3.0
2-5-L	TVA	2.5	2.5	1504	1700	1.14	36.4	0.6	5.0	2.4 ± 0.6[d]	33 ± 9	--	0.300	0.0049	10.0	3.0
2-5-M	TVA	2.5	2.0	1504	1700	1.14	35.7	0.6	4.5	2.2 ± 0.6[d]	29 ± 8	--	0.300	0.0049	10.0	3.0
2-4-L	TVA	3	3.1	1506	1700	1.7	42.0	0.6	7.3	4.0	55	28	0.303	0.0053	10.2	2.6
2-4-M	TVA	2.5	2.5	1506	1700	1.7	41.5	0.6	6.8	3.8	52	25	0.303	0.0053	10.2	2.6
11-4-E	TVA	1.5	1.1	1800	2700	0.18	41.0	0.4	7.2	4.1	56	23	0.304	0.0028	10.2	2.8
11-4-F	TVA	1.5	1.5	1800	2700	0.18	41.9	0.4	5.6	3.1	42	25	0.304	0.0028	10.2	2.8
10-24-N	TVA	3	1.43	1802	2700	0.58	45.2	0.8	21.5	11.1	150	62	0.303	0.0035	10.2	2.8
10-24-O	TVA	3	0.43	1802	2700	0.58	42.1	0.7	22.0	12.1	165	50	0.303	0.0035	10.2	2.8

BATTELLE MEMORIAL INSTITUTE - COLUMBUS LABORATORIES

TABLE C-1. (Continued)

Run Number	Stone Number[a]	Injection Data: Time, min	Injection Data: Rate, g/min	Gas Temp, °F	Reynolds Number	Residence Time, sec	Product Analysis[b]: Ca	Product Analysis[b]: Mg	Product Analysis[b]: $SO_4^=$	Percent CaO Utilization	SO_3, mg per gram calcine	Calculated Percent Calcination	Gas Analysis, volume percent[c]: SO_2	Gas Analysis, volume percent[c]: SO_3	Gas Analysis, volume percent[c]: CO_2	Gas Analysis, volume percent[c]: O_2
1-28-V	TVA	1.5	4.0	1803	2500	0.95	51.8	0.7	15.0	6.7	92	76	0.303	0.0038	10.6	2.4
1-28-W	TVA	1.5	3.5	1803	2500	0.95	50.7	0.7	15.3	7.0	95	73	0.303	0.0038	10.6	2.4
11-7-L	TVA	2	1.4	2100	3900	0.10	42.5	0.6	10.0	5.5	74	34	0.298	0.0023	11.0	2.6
11-7-M	TVA	2	1.0	2100	3900	0.10	40.4	0.4	7.1	4.1	56	19	0.298	0.0023	11.0	2.6
10-30-R	TVA	3	?	2100	3800	0.34	48.6	0.9	18.0	8.6	117	69	0.299	0.0029	10.0	3.0
10-30-S	TVA	3	1.5	2100	3800	0.34	55.0	11.0	18.9	8.0	109	89	0.299	0.0029	10.0	3.0
11-19-J	TVA	4	1.8	2100	3800	0.50	49.9	0.7	13.0	6.1	82	87	0.302	0.0026	10.2	2.6
11-19-K	TVA	4	1.7	2100	3800	0.50	66.8	0.7	16.0	8.2 ± 2.0[d]	111 ± 28	--	0.302	0.0026	10.2	2.6
2-6-CC	1360	1	1.8	1500	1720	0.36	25.6	8.0	3.0	1.6 ± 0.4[d]	19 ± 4	--	0.300	0.0049	10.0	3.0
2-6-DD	1360	1	1.3	1500	1720	0.36	23.5	7.9	3.2	1.7 ± 0.4[d]	20 ± 5	--	0.300	0.0049	10.0	3.0
2-5-J	1360	2	3.0	1504	1700	1.14	25.4	8.1	5.4	3 ± 0.7[d]	34 ± 8	--	0.300	0.0049	10.0	3.0
2-5-K	1360	3	2.2	1504	1700	1.14	24.6	7.8	6.6	3.7 ± 0.8[d]	42 ± 10	--	0.300	0.0049	10.0	3.0
2-4-J	1360	3	3.4	1506	1700	1.7	29.4	8.4	8.3	4.7 ± 1[d]	53 ± 12	--	0.303	0.0053	10.2	2.6
2-4-K	1360	2.5	2.7	1506	1700	1.7	29.2	8.8	7.8	4.4 ± 1[d]	50 ± 11	--	0.303	0.0053	10.2	2.6
2-6-C	1360	2.5	2.9	1500	1700	1.72	27.5	8.9	7.4	4.2 ± 0.9[d]	47 ± 11	--	0.300	0.0049	10.0	3.0
2-6-D	1360	2.5	2.9	1500	1700	1.72	27.5	9.0	6.7	3.7 ± 0.8[d]	42 ± 10	--	0.300	0.0049	10.0	3.0
11-4-A	1360	1.5	1.6	1800	2700	0.18	22.5	9.3	11.7	6.7 ± 1.4[d]	76 ± 17	--	0.304	0.0028	10.2	2.8
11-4-B	1360	1.5	1.6	1800	2700	0.18	32.1	9.5	10.6	6.1 ± 1.4[d]	68 ± 12	--	0.304	0.0028	10.2	2.8
10-24-J	1360	3	0.90	1802	2700	0.58	28.3	10.9	19.1	15.7	177	0 (-18)	0.303	0.0035	10.2	2.8
10-24-K	1360	3	1.40	1802	2700	0.58	30.6	11.3	21.0	16.0	180	6	0.303	0.0035	10.2	2.8
1-28-T	1360	1.5	4.6	1803	2500	0.95	40.3	9.9	17.6	10.2	115	62	0.303	0.0038	10.6	2.4
1-28-U	1360	1.5	5.2	1803	2500	0.95	40.0	10.2	16.3	9.5	107	59	0.303	0.0038	10.6	2.4
11-7-J	1360	2	1.8	2100	3900	0.10	24.2	8.0	10.2	5.8 ± 1.3[d]	66 ± 15	--	0.298	0.0023	11.0	2.6
11-7-K	1360	2	1.6	2100	3900	0.10	36.5	6.3	9.1	5.8	65	27	0.298	0.0023	11.0	2.6
10-30-N	1360	3	1.5	2100	3800	0.34	22.2	12.9	22.2	13.5 ± 2.7[d]	150 ± 30	--	0.299	0.0029	10.0	3.0
10-30-O	1360	3	1.3	2100	3800	0.34	26.8	12.3	24.5	15.1 ± 3.0[d]	170 ± 35	--	0.299	0.0029	10.0	3.0
11-19-L	1360	4	1.8	2100	3800	0.50	39.5	8.1	17.6	10.4	117	58	0.302	0.0026	10.2	2.6
11-19-M	1360	4	1.9	2100	3800	0.50	49.4	10.1	21.0	12.7 ± 2.6[d]	144 ± 30	--	0.302	0.0026	10.2	2.6
2-12-A	1337	2	1.0	1305	1600	0.44	20.0	12.4	2.1	1.5 ± 0.3[d]	12 ± 2	--	0.300	0.0005	10.0	3.0
2-12-B	1337	2	0.8	1305	1600	0.44	20.1	12.4	1.8	1.3 ± 0.2[d]	10 ± 1	--	0.300	0.0005	10.0	3.0

TABLE C-1. (Continued)

Run Number	Stone Number[a]	Injection Data: Time, min	Injection Data: Rate, g/min	Gas Temp, °F	Reynolds Number	Residence Time, sec	Product Analysis[b]: Ca	Product Analysis[b]: Mg	Product Analysis[b]: $SO_4^=$	Percent CaO Utilization	SO_3, mg per gram calcine	Calculated Percent Calcination	Gas Analysis, volume percent[c]: SO_2	Gas Analysis, volume percent[c]: SO_3	Gas Analysis, volume percent[c]: CO_2	Gas Analysis, volume percent[c]: O_2
2-12-L	1337	3.5	2.05	1339	1600	1.39	22.2	12.6	2.6	7.9 ± 0.3[d]	15 ± 3	--	0.300	0.0005	10.0	3.0
2-12-M	1337	3.5	2.0	1339	1600	1.39	22.1	12.4	2.6	7.9 ± 0.3[d]	15 ± 3	--	0.300	0.0005	10.0	3.0
2-12-N	1337	4	3.0	1372	1600	2.1	21.7	12.4	3.1	2.3 ± 0.4[d]	18 ± 3	--	0.300	0.0005	10.0	3.0
2-12-O	1337	4	2.5	1372	1600	2.1	21.9	12.5	3.2	2.3 ± 0.4[d]	18 ± 3	--	0.300	0.0005	10.0	3.0
2-6-T	1337	1	2.7	1500	1700	0.36	21.6	13.0	~0	--	--	--	0.300	0.0049	10.0	3.0
2-6-U	1337	1	1.5	1500	1700	0.36	21.4	13.0	~0	--	--	--	0.300	0.0049	10.0	3.0
2-5-N	1337	3.5	1.9	1504	1700	1.14	21.1	13.1	5.9	4.8 ± 0.7[d]	34 ± 6	--	0.300	0.0049	10.0	3.0
2-5-O	1337	3	2	1504	1700	1.14	21.3	13.4	5.6	4.2 ± 0.7[d]	33 ± 6	--	0.300	0.0049	10.0	3.0
2-4-N	1337	1.5	2.8	1506	1700	1.7	25.2	14.4	9.8	9.0	71	-6	0.303	0.0053	10.2	2.6
2-4-O	1337	2.5	2.6	1506	1700	1.7	26.2	14.8	11.0	9.8	77	10	0.303	0.0053	10.2	2.6
11-1-C	1337	1.5	1.8	1800	2600	0.19	26.0	14.8	11.7	10.4	82	9	0.301	0.0026	11.0	2.5
11-1-D	1337	1	1.3	1800	2600	0.19	23.8	14.6	10.4	10.2	80	24	0.301	0.0026	11.0	2.5
10-23-G	1337	3	3.30	1800	2700	0.58	26.8	19.8	19.5	16.9	133	37	0.300	0.0029	10.4	2.9
10-23-H	1337	3	1.20	1800	2700	0.58	27.0	20.3	25.2	21.7	171	52	0.300	0.0029	10.4	2.9
1-28-A	1337	2	2.7	1803	2500	0.95	33.1	20.0	20.6	14.5	114	95	0.303	0.0038	10.6	2.4
1-28-B	1337	3	2.3	1803	2500	0.95	33.0	19.9	22.7	16.0	126	98	0.303	0.0038	10.6	2.4
10-4-A	1337	3	0.95	1902	3200	0.46	28.0	17.8	19.0	15.8	124	48	0.300	0.0032	10.0	2.8
10-4-B	1337	3	1.00	1902	3200	0.46	NS[c]	NS	17.8	14.1 ± 2.2[d]	111 ± 17	--	0.300	0.0032	10.0	2.8
11-6-A	1337	1.5	0.9	2006	3500	0.12	15.5	17.1	12.5	9.6 ± 1.6[d]	75 ± 12	--	0.300	0.0028	10.0	2.5
11-6-B	1337	1.5	1.7	2006	3500	0.12	24.5	17.2	11.8	9.1 ± 1.5[d]	71 ± 11	--	0.300	0.0028	10.0	2.5
10-28-C	1337	3	1.03	1996	3400	0.40	29.2	19.4	25.3	20.1	158	73	0.295	0.0029	10.8	2.6
10-28-D	1337	3	1.90	1996	3400	0.40	30.0	19.5	27.0	20.9	164	84	0.295	0.0029	10.8	2.6
1-6-J	1337	2	5.5	2000	3300	0.61	34.4	20.6	22.1	14.9	117	106	0.302	0.0033	10.9	2.7
1-6-K	1337	2	2.8	2000	3300	0.61	34.3	20.6	22.8	15.4	121	107	0.302	0.0033	10.9	2.7
10-30-A	1337	3	1.0	2100	3800	0.34	19.8	19.2	24.1	19.2[e]	151	71	0.299	0.0029	10.0	3.0
10-30-B	1337	3	0.76	2100	3800	0.34	27.7	17.9	24.0	20.1	158	56	0.299	0.0029	10.0	3.0
2-12-C	1337C	3	1.7	1305	1600	0.44	39.7	23.3	4.0	2.3	18	108	0.300	0.0005	10.0	3.0
2-12-D	1337C	1.5	0.55	1305	1600	0.44	38.8	23.0	4.3	2.6	20	104	0.300	0.0005	10.0	3.0
2-12-J	1337C	5	0.9	1339	1600	1.39	40.4	23.7	6.5	3.7	29	116	0.300	0.0005	10.0	3.0
2-12-K	1337C	4	1.5	1339	1600	1.39	39.8	22.7	6.4	3.7	29	113	0.300	0.0005	10.0	3.0

TABLE C-1. (Continued)

Run Number	Stone Number[a]	Injection Data: Time, min	Injection Data: Rate, g/min	Gas Temp, °F	Reynolds Number	Residence Time, sec	Product Analysis[b]: Ca	Product Analysis[b]: Mg	Product Analysis[b]: $SO_4^=$	Percent CaO Utilization	SO_3, mg per gram calcine	Calculated Percent Calcination	Gas Analysis, volume percent[c]: SO_2	Gas Analysis, volume percent[c]: SO_3	Gas Analysis, volume percent[c]: CO_2	Gas Analysis, volume percent[c]: O_2
2-12-P	1337C	6	0.95	1372	1600	2.1	39.4	23.1	7.9	4.7	37	113	0.300	0.0005	10.0	3.0
2-12-Q	1337C	6	0.95	1372	1600	2.1	39.7	23.3	7.7	4.5	35	114	0.300	0.0005	10.0	3.0
2-6-R	1337C	1	0.75	1500	1700	0.36	40.0	24.2	3.5	2.0	16	109	0.300	0.0049	10.0	3.0
2-6-S	1337C	1	1.0	1500	1700	0.36	40.5	23.9	3.2	1.8	14	112	0.300	0.0049	10.0	3.0
2-5-P	1337C	2.5	1.3	1504	1700	1.14	35.9	21.3	9.6	6.2	49	95	0.300	0.0049	10.0	3.0
2-5-Q	1337C	4	1.5	1504	1700	1.14	36.4	22.4	10.1	6.5	51	99	0.300	0.0049	10.0	3.0
2-4-P	1337C	2.5	1.9	1506	1700	1.7	38.8	22.4	11.2	6.7	53	114	0.303	0.0053	10.2	2.6
2-4-Q	1337C	2.5	1.5	1506	1700	1.7	37.9	22.3	9.3	5.7	45	106	0.303	0.0053	10.2	2.6
11-4-R	1337C	2	1.0	1800	2700	0.18	33.9	21.1	6.6	4.5	36	75	0.304	0.0028	10.2	2.8
11-4-S	1337C	2	1.3	1800	2700	0.18	35.6	21.7	8.7	5.7	47	91	0.304	0.0028	10.2	2.8
10-23-C	1337C	3	0.55	1800	2700	0.58	34.6	13.5	13.5	9.1	71	93	0.300	0.0029	10.4	2.9
10-23-D	1337C	3	0.70	1800	2700	0.58	33.3	21.6	17.4	12.1	95	90	0.300	0.0029	10.4	2.9
1-28-L	1337C	3	1.5	1803	2500	0.95	38.7	22.4	5.8	3.5	27	106	0.303	0.0038	10.6	2.4
1-28-M	1337C	3	1.0	1803	2500	0.95	38.4	22.4	7.7	4.7	37	107	0.303	0.0038	10.6	2.4
11-6-L	1337C	2	1.3	2006	3500	0.12	30.3	21.6	8.1	5.7[e]	45	70	0.300	0.0028	10.0	2.5
11-6-M	1337C	2	0.75	2006	3500	0.12	37.3	20.4	12.0	7.5	52	102	0.300	0.0028	10.0	2.5
10-28-E	1337C	3	0.60	1996	3400	0.40	32.2	19.3	18.7	13.5	106	85	0.295	0.0029	10.8	2.6
10-28-F	1337C	3	1.00	1996	3400	0.40	46.2	21.4	17.8	9.0	70	158	0.295	0.0029	10.8	2.6
1-6-L	1337C	3	0.8	2000	3300	0.61	36.0	21.8	16.8	10.8	85	107	0.302	0.0033	10.9	2.7
1-6-M	1337C	3.5	1.05	2000	3300	0.61	36.9	21.6	13.3	8.4	65	107	0.302	0.0033	10.9	2.7
10-30-E	1337C	3	0.9	2100	3800	0.34	37.4	19.7	13.5	8.4	66	110	0.299	0.0029	10.0	3.0
10-30-F	1337C	3	1.1	2100	3800	0.34	35.8	22.8	15.2	9.9	76	104	0.299	0.0029	10.0	3.0
2-6-J	1337MH	4	0.75	1500	1700	0.36	34.5	22.0	9.0	6.1	48	84	0.300	0.0049	10.0	3.0
2-6-K	1337MH	3	0.33	1500	1700	0.36	33.7	20.9	9.2	6.3	50	79	0.300	0.0049	10.0	3.0
2-5-X	1337MH	4	1.2	1504	1700	1.14	34.2	22.1	12.7	8.6	68	88	0.300	0.0049	10.0	3.0
2-5-Y	1337MH	4	1.3	1504	1700	1.14	34.0	21.9	14.3	9.8	77	90	0.300	0.0049	10.0	3.0
2-4-V	1337MH	2.5	1.5	1506	1700	1.7	35.5	21.6	11.9	7.8	61	96	0.303	0.0053	10.2	2.6
2-4-W	1337MH	3	1.5	1508	1700	1.7	32.6	20.4	17.2	12.3	96	85	0.303	0.0053	10.2	2.6
2-6-G	1337MH	5	0.9	1500	1700	1.72	33.7	21.4	19.2	13.2	104	97	0.300	0.0049	10.0	3.0
2-6-H	1337MH	5	0.8	1500	1700	1.72	33.2	20.5	20.7	14.5	113	96	0.300	0.0049	10.0	3.0

TABLE C-1. (Continued)

Run Number	Stone Number[a]	Injection Data: Time, min	Injection Data: Rate, g/min	Gas Temp, °F	Reynolds Number	Residence Time, sec	Product Analysis[b]: Ca	Product Analysis[b]: Mg	Product Analysis[b]: $SO_4^{=}$	Percent CaO Utilization	SO_3, mg per gram calcine	Calculated Percent Calcination	Gas Analysis, volume percent[c]: SO_2	Gas Analysis, volume percent[c]: SO_3	Gas Analysis, volume percent[c]: CO_2	Gas Analysis, volume percent[c]: O_2
11-4-L	1337MH	2	1.0	1800	2700	0.18	32.3	19.5	13.9	10.0	79	76	0.304	0.0028	10.2	2.8
11-4-M	1337MH	2	1.0	1800	2700	0.18	39.9	21.8	13.3	9.3[e]	73	82	0.304	0.0028	10.2	2.8
10-23-A	1337MH	3	0.30	1800	2700	0.58	26.9	20.9	18.3	15.8	124	35	0.300	0.0029	10.4	2.9
10-23-B	1337MH	3	0.70	1800	2700	0.58	33.4	22.0	14.0	9.7	77	85	0.300	0.0029	10.4	2.9
1-28-E	1337MH	5	1.0	1803	2500	0.95	37.1	22.3	13.0	8.1	64	108	0.303	0.0038	10.6	2.4
1-28-F	1337MH	4	0.9	1803	2500	0.95	35.2	21.0	18.1	12.0	94	105	0.303	0.0038	10.6	2.4
11-6-E	1337MH	1.5	1.8	2006	3500	0.12	27.7	19.3	8.7	6.9	54	40	0.300	0.0028	10.0	2.5
11-6-F	1337MH	1.5	?	2006	3500	0.12	19.9	18.0	6.3	4.7 ± 0.8[d]	36 ± 6	--	0.300	0.0028	10.0	2.5
10-28-J	1337MH	2	1.70	1996	3400	0.40	33.5	21.0	19.1	13.2	104	95	0.295	0.0029	10.8	2.6
10-28-K	1337MH	2	1.10	1996	3400	0.40	32.8	20.7	23.2	16.4	129	98	0.295	0.0029	10.8	2.6
1-6-C	1337MH	3	0.9	2000	3300	0.61	35.5	21.5	18.4	12.1	95	107	0.302	0.0033	10.9	2.7
1-6-D	1337MH	3	1.2	2000	3300	0.61	36.2	21.4	19.4	12.5	98	113	0.302	0.0033	10.9	2.7
11-7-P	1337MH	2	1.1	2100	3900	0.10	46.8	21.4	8.0	5.7[e]	45	68	0.298	0.0023	11.0	2.6
11-7-Q	1337MH	3	1.1	2100	3900	0.10	46.2	20.5	10.1	7.5[e]	59	60	0.298	0.0023	11.0	2.6
11-13-C	1337MH	3	1.3	2102	3600	0.36	39.7	19.8	18.8	14.5[e]	114	68	0.300	0.0028	10.2	2.8
11-13-D	1337MH	3	1.3	2102	3600	0.36	43.3	20.0	20.7	15.8[e]	124	75	0.300	0.0028	10.2	2.8
11-19-P	1337MH	4	1.0	2100	3800	0.50	40.6	21.3	14.2	10.2[e]	80	78	0.302	0.0026	10.2	2.6
11-19-Q	1337MH	5	0.8	2100	3800	0.50	31.0	20.7	16.5	12.4	97	71	0.302	0.0026	10.2	2.6
2-6-N	1337DH	2	0.5	1500	1700	0.36	32.1	19.3	12.3	8.9	70	72	0.300	0.0049	10.0	3.0
2-6-O	1337DH	1.5	0.9	1500	1700	0.36	32.3	19.6	12.3	8.9	70	73	0.300	0.0049	10.0	3.0
2-5-T	1337DH	5	1.0	1504	1700	1.14	32.8	20.9	18.2	12.9	101	88	0.300	0.0049	10.0	3.0
2-5-U	1337DH	5	0.8	1504	1700	1.14	32.6	20.3	20.7	14.8	116	91	0.300	0.0049	10.0	3.0
2-4-T	1337DH	2.5	1.9	1506	1700	1.7	34.5	20.9	17.0	11.5	90	98	0.303	0.0053	10.2	2.6
2-4-U	1337DH	3	2.9	1506	1700	1.7	33.3	20.0	21.5	15.0	118	98	0.303	0.0053	10.2	2.6
11-4-N	1337DH	2	1.0	1800	2700	0.18	25.4	17.8	22.3	19.1[e]	150	46	0.304	0.0028	10.2	2.8
11-4-O	1337DH	2	0.8	1800	2700	0.18	21.8	17.2	23.4	20.8[e]	163	39	0.304	0.0028	10.2	2.8
10-23-E	1337DH	3	0.80	1800	2700	0.58	26.3	20.8	26.9	23.8	187	48	0.300	0.0029	10.4	2.9
10-23-F	1337DH	3	1.10	1800	2700	0.58	28.7	19.7	24.5	19.9	156	67	0.300	0.0029	10.4	2.9
1-28-G	1337DH	4	1.6	1803	2500	0.95	35.8	21.5	15.4	10.0	79	104	0.303	0.0038	10.6	2.4
1-28-H	1337DH	3	1.0	1803	2500	0.95	35.8	21.5	15.4	10.0	79	104	0.303	0.0038	10.6	2.4

TABLE C-1. (Continued)

Run Number	Stone Number[a]	Injection Data: Time, min	Injection Data: Rate, g/min	Gas Temp, °F	Reynolds Number	Residence Time, sec	Product Analysis[b]: Ca	Product Analysis[b]: Mg	Product Analysis[b]: $SO_4^=$	Percent CaO Utilization	SO_3, mg per gram calcine	Calculated Percent Calcination	Gas Analysis, volume percent[c]: SO_2	Gas Analysis, volume percent[c]: SO_3	Gas Analysis, volume percent[c]: CO_2	Gas Analysis, volume percent[c]: O_2
11-6-G	1337DH	2	0.8	2006	3500	0.12	20.4	17.2	17.9	15.9[e]	125	26	0.300	0.0028	10.0	2.5
11-6-H	1337DH	2	0.9	2006	3500	0.12	21.4	16.2	14.8	13.6[e]	107	8	0.300	0.0028	10.0	2.5
10-28-L	1337DH	2	2.00	1996	3400	0.40	33.9	20.0	26.8	18.4	144	112	0.295	0.0029	10.8	2.6
10-28-M	1337DH	2	1.40	1996	3400	0.40	29.2	18.9	27.0	21.5	169	77	0.295	0.0029	10.8	2.6
1-6-A	1337DH	3	0.5	2000	3300	0.61	34.0	20.1	23.1	15.8	124	106	0.302	0.0033	10.9	2.7
1-6-B	1337DH	3	0.7	2000	3300	0.61	34.4	20.5	22.6	15.3	120	107	0.302	0.0033	10.9	2.7
11-7-R	1337DH	2	1.1	2100	3900	0.10	33.2	18.5	11.8	8.3	65	79	0.298	0.0023	11.0	2.6
11-7-S	1337DH	2	0.9	2100	3900	0.10	34.7	20.3	15.9	8.4	66	92	0.298	0.0023	11.0	2.6
11-13-E	1337DH	3	1.4	2102	3600	0.36	35.3	17.3	25.6	22.6[e]	177	45	0.300	0.0028	10.2	2.8
11-13-F	1337DH	3	1.3	2102	3600	0.36	39.8	18.9	25.2	20.3[e]	160	69	0.300	0.0028	10.2	2.8
11-19-R	1337DH	4	1.0	2100	3800	0.50	40.8	20.6	21.4	15.9[e]	125	83	0.302	0.0026	10.2	2.6
11-19-S	1337DH	4	0.7	2100	3800	0.50	31.8	20.9	19.2	14.0	110	83	0.302	0.0026	10.2	2.6
10-10-C	1337[f]	4	0.80	1903	3100	0.47	31.3	18.5	18.7	13.9	109	78	0.303	0.0028	10.2	2.8
10-10-D	1337[f]	4	0.65	1903	3100	0.47	31.2	17.4	18.9	14.1	107	77	0.303	0.0028	10.2	2.8
1-13-P	1337[i]	1.5	1.35	1903	2900	0.51	33.9	20.8	18.9	13.0	101	97	0.296	0.0036	10.6	2.7
1-13-Q	1337[i]	1	2	1903	2900	0.51	33.7	20.2	19.5	13.5	105	97	0.296	0.0036	10.6	2.7
10-18-J	1337[g]	4	0.70	1900	3100	0.47	31.7	19.4	29.3	21.5	169	100	0.297	0.0027	10.2	2.8
10-18-K	1337[g]	4	0.55	1900	3100	0.47	NS	NS	30.9	26.6 ± 3.5[d]	209 ± 27	--	0.297	0.0027	10.2	2.8
1-13-V	1337[j]	2	1.8	1903	2900	0.51	32.3	17.6	23.9	17.2	135	95	0.293	0.0032	10.2	3.0
1-13-W	1337[j]	2	1.8	1903	2900	0.51	31.9	17.8	24.1	17.6	138	93	0.293	0.0032	10.2	3.0
1-13-G	1337[h]	1.5	1.3	1903	2900	0.51	34	20.5	17.8	12.1	95	96	0.296	0.0036	10.6	2.7
1-13-H	1337[h]	1.5	1.3	1903	2900	0.51	33.4	20.1	19.6	13.6	107	95	0.296	0.0036	10.6	2.7
10-10-G	1373[g]	4	0.60	1903	3100	0.47	51.9	2.0	17.8	8.0	98	94	0.303	0.0028	10.2	2.8
10-10-H	1373[g]	4	0.45	1903	3100	0.47	52.0	1.9	18.8	8.4	103	95	0.303	0.0028	10.2	2.8
1-13-N	1373[i]	2	1	1903	2900	0.51	48.1	2.8	27.7	13.4	164	94	0.296	0.0036	10.6	2.7
1-13-O	1373[i]	2	1	1903	2900	0.51	48.2	3.1	25.9	12.5	153	92	0.296	0.0036	10.6	2.7
1-13-T	1373[j]	2	2.5	1903	2900	0.51	46.0	2.9	25.2	12.7	156	84	0.293	0.0032	10.2	3.0
1-13-U	1373[j]	2	2.5	1903	2900	0.51	47.3	2.0	23.0	11.3	138	86	0.293	0.0032	10.2	3.0
1-13-E	1373[h]	1.0	1.4	1903	2900	0.51	49.4	3.3	20.8	9.8	120	90	0.296	0.0036	10.6	2.7
1-13-F	1373[h]	1.0	1.0	1903	2900	0.51	48.9	3.6	22.0	10.4	128	90	0.296	0.0036	10.6	2.7

TABLE C-1. (Continued)

Run Number	Stone Number[a]	Injection Data: Time, min	Injection Data: Rate, g/min	Gas Temp, °F	Reynolds Number	Residence Time, sec	Product Analysis[b]: Ca	Product Analysis[b]: Mg	Product Analysis[b]: $SO_4^=$	Percent CaO Utilization	SO_3, mg per gram calcine	Calculated Percent Calcination	Gas Analysis, volume percent[c]: SO_2	Gas Analysis, volume percent[c]: SO_3	Gas Analysis, volume percent[c]: CO_2	Gas Analysis, volume percent[c]: O_2
10-10-E	1373[f]	4	1.50	1903	3100	0.47	46.6	2.6	11.1	5.5	68	68	0.303	0.0028	10.2	2.8
10-10-F	1373[f]	4	1.25	1903	3100	0.47	46.5	2.5	11.1	5.6	68	67	0.303	0.0028	10.2	2.8
2-6-V	1373	1	3.5	1500	1700	0.36	35.4	2.4	1.9	1.2	15	-5	0.300	0.0049	10.0	3.0
2-6-W	1373	1	1	1500	1700	0.36	34.7	2.3	2.9	1.9	24	-9	0.300	0.0049	10.0	3.0
2-5-E	1373	2.5	2.2	1504	1700	1.14	33.1	2.1	5.8	3 ± 0.7[d]	37 ± 9	--	0.300	0.0049	10.0	3.0
2-5-F	1373	2.5	2.7	1504	1700	1.14	31.5	2.0	5.0	2.6 ± 0.6[d]	32 ± 8	--	0.300	0.0049	10.0	3.0
2-4-C	1373	3	2.3	1506	1700	1.7	38.2	2.5	10.2	6.2	76	26	0.303	0.0053	10.2	2.6
2-4-D	1373	4	1.9	1506	1700	1.7	38.2	2.5	13.1	8.0	98	31	0.303	0.0053	10.2	2.6
11-1-A	1373	1.5	1.25	1800	2600	0.19	29.6	3.4	10.6	5.7 ± 1.3[d]	70 ± 17	--	0.301	0.0026	11.0	2.5
11-1-B	1373	1.5	1.85	1800	2600	0.19	37.8	3.3	11.0	5.9 ± 1.4[d]	72 ± 17	--	0.301	0.0026	11.0	2.5
10-24-E	1373	3	0.80	1802	2700	0.58	36.4	3.4	20.2	12.9	159	32	0.303	0.0035	10.2	2.8
10-24-F	1373	3	0.70	1802	2700	0.58	33.3	4.1	23.1	16.1	198	18	0.303	0.0035	10.2	2.8
1-28-P	1373	2	4.5	1803	2500	0.95	46.6	2.7	19.5	9.7	120	79	0.303	0.0038	10.6	2.4
1-28-Q	1373	1	3.7	1803	2500	0.95	46.1	2.4	18.2	9.2	113	75	0.303	0.0038	10.6	2.4
10-18-A	1373	3	0.75	1900	3100	0.47	41.4	2.8	18.8	10.6	130	56	0.297	0.0027	10.2	2.8
10-18-B	1373	3	0.80	1900	3100	0.47	43.1	2.1	23.6	12.7	156	71	0.297	0.0027	10.2	2.8
11-7-A	1373	2	1.6	2100	3900	0.10	40.8	2.1	8.1	4.6	57	37	0.298	0.0023	11.0	2.6
11-7-B	1373	2	1.8	2100	3900	0.10	38.4	1.7	6.1	3.7	45	21	0.298	0.0023	11.0	2.6
10-30-G	1373	3	1.6	2100	3800	0.34	43.5	3.4	20.8	11.1	137	68	0.299	0.0029	10.0	3.0
10-30-H	1373	3	1.1	2100	3800	0.34	48.1	3.4	21.0	10.1	125	86	0.299	0.0029	10.0	3.0
11-19-C	1373	3	1.3	2100	3800	0.50	45	2.4	16.9	8.7	107	69	0.302	0.0026	10.2	2.6
11-19-D	1373	3	1.3	2100	3800	0.50	66.8	1.8	16.4	9.1 ± 2[d]	111 ± 25	--	0.302	0.0026	10.2	2.6

(a) Stone numbers alone indicate raw stone. Suffixes on numbers indicate other chemical states as follows: C-calcined; H-hydrate; MH-monohydrate; DH-dihydrate. (all -140 + 200 mesh unless otherwise noted).
(b) Weight percent. $SO_4^=$ is expressed as $CaSO_4 \cdot 2H_2O$.
(c) CO_2 and O_2 by Orsat, SO_2 and SO_3 by titration.
(d) Calculated as indicated in Summary Report dated August 30, 1968. Error range indicated is only that resulting from computational procedure.
(e) Calculated from Mg analysis.
(f) -100 + 200 mesh.
(g) -270 + 325 mesh.
(h) 20-40 micron.
(i) 10-20 micron.
(j) 5-10 micron.

APPENDIX D

TREATMENT OF DATA

APPENDIX D

TREATMENT OF DATA

Analytical data obtained on reacted samples are in the form of weight percentage of $CaSO_4 \cdot 2H_2O$, calcium and magnesium. These data are transposed to more useful forms as follows:

Let

y = weight fraction $CaSO_4 \cdot 2H_2O$

x = weight fraction calcium

R = weight of CaO which has reacted with SO_2 per gram of sample

U = weight of calcium compounds which have not reacted, expressed as CaO, per gram of sample

z = fractional utilization of total calcium in sample

g = weight of nonreactive material per gram of sample

M = average molecular weight of unreacted CaO species ($CaCO_3$, CaO, etc.)

S = grams of SO_3 sorbed per gram of completely calcined stone

C = fraction of $CaCO_3$ which has been calcined.

For computational purposes, it is assumed that

(1) Only CaO reacts with the SO_2.

(2) Unreacted CaO is present as either CaO or $CaCO_3$.

(3) The analyses of calcined stones obtained by Bituminous Coal Research, Inc., apply to currently used specimens (see Summary Report dated August 30, 1968).

(4) Any $MgCO_3$ is completed calcined.

Then

$$g = K(R + U), \text{ where K can be calculated from the BCR data,} \quad (1)$$

$$y = R(172/56), \quad (2)$$

and

$$x = (R+U)(40/56); \quad (3)$$

therefore,

$$z = (40/172)(y/x) \quad (4)$$

and

$$S = \frac{(80/56)\,R}{R+U+g} = \frac{80z}{56(1+K)} \quad . \tag{5}$$

Now

$$g = 1 - R(172/56) - U(M/56) \; ; \tag{6}$$

using Equation (1) for g, and solving Equations (2), (3), and (4) for R and U in terms of y and z, Equation (6) can be rearranged to yield

$$M = \frac{172(1-y) - 56K(y/z)}{y/z - y} \quad . \tag{7}$$

Then, to evaluate the percent calcination,

let p = the weight of CaO per gram of sample which has not reacted

and

q = the weight of $CaCO_3$ remaining in 1 gram of sample.

Thence,

$$C = (R + p)/(R + U) \tag{8}$$

and M may be defined as

$$M = (p + q)/(p/56 + q/100) \quad . \tag{9}$$

Since

$$q = (U - p)(100/56) \; , \tag{10}$$

p may be evaluated in terms of U and M :

$$p = (100-M)U/44 \; . \tag{11}$$

Substituting the value of p from Equation (11) in Equation (8) yields

$$C = \frac{R + \left(\frac{100-M}{44}\right) U}{R + U} \quad .$$

But R/(R+U) = z and U/(R+U) = 1-z .

Therefore,

$$C = z + \left(\frac{100-M}{44}\right)(1-z) \tag{12}$$

The calculated values of the fractional utilization of calcium, z, in the sample and the SO_3 pickup, S, thus depend upon the measured quantities x and y in a way such that minor inaccuracies in x, the calcium analysis, affect the values of z and S more strongly than do comparable inaccuracies in y, the sulfate analysis. This sensitivity to the accuracy of the calcium analysis is accentuated in the calculation of percentage calcination because of the ratio of differences involved in the calculation of M. With dolomites, in which there is less calcium to begin with, the sensitivity to errors in analysis is increased further. As an example, Figure D-1 shows the calculated values of percentage calcination as a function of weight percent calcium for a relatively pure dolomite and a relatively pure limestone at two levels of sulfate content. It can be seen that the calculated value of percentage calcination for a dolomitic sample is strongly dependent upon calcium analysis, especially for low true calcination percentages.

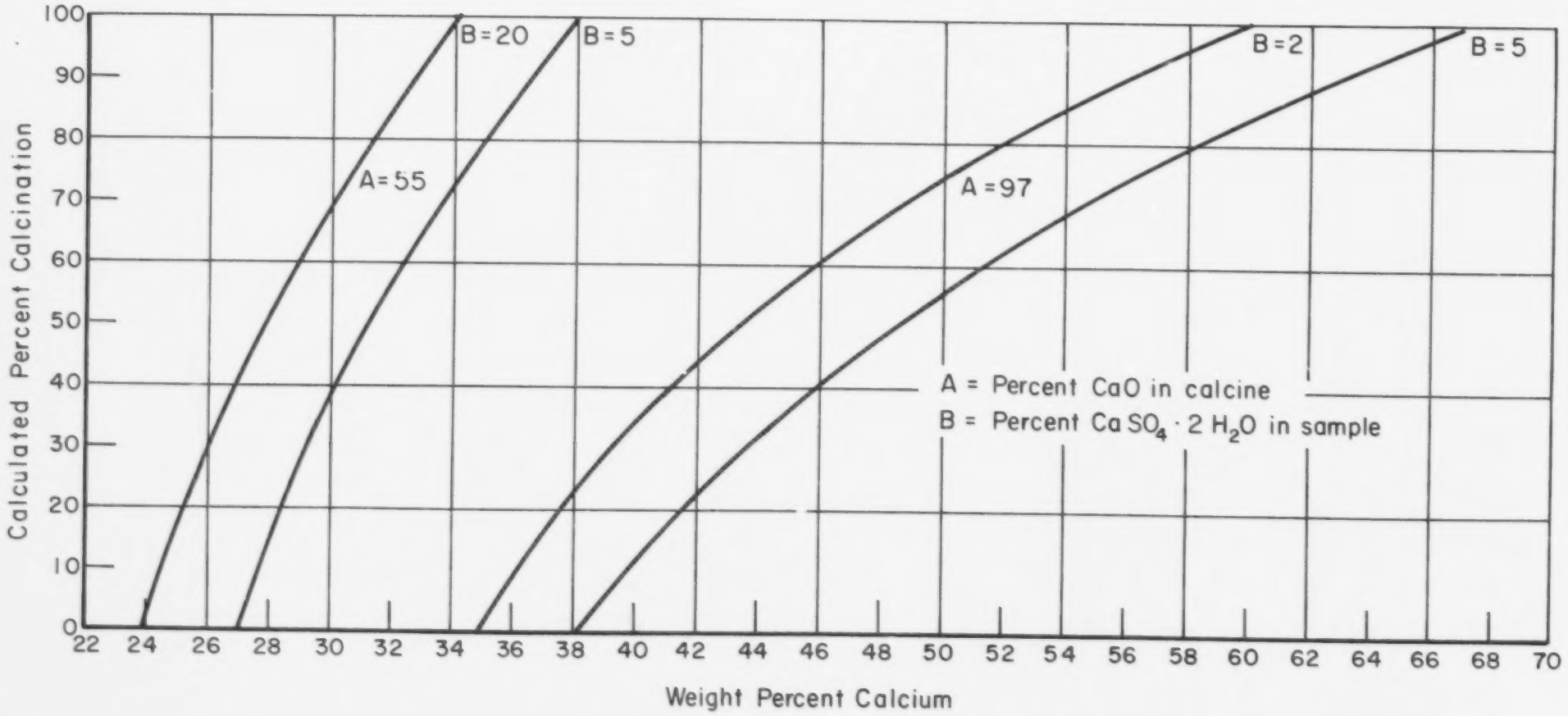

FIGURE D-1. DEPENDENCE OF CALCULATED PERCENT CALCINATION ON ANALYSIS ACCURACY

APPENDIX E

TEMPERATURE DEPENDENCE OF RATE DATA

APPENDIX E

TEMPERATURE DEPENDENCE OF RATE DATA

Examples of Arrhenius plots for the apparent rates of reaction of stones No. 10 and No. 11 are given in the main body of this report. Arrhenius plots for the remaining stones and limes studied during this contract period are shown in Figures E-1 through E-7 of this Appendix. As stated in the text, apparent activation energies associated with these plots cannot at this time be related to individual chemical or physical processes, but, rather, the plots serve as a convenient means of organization of the data.

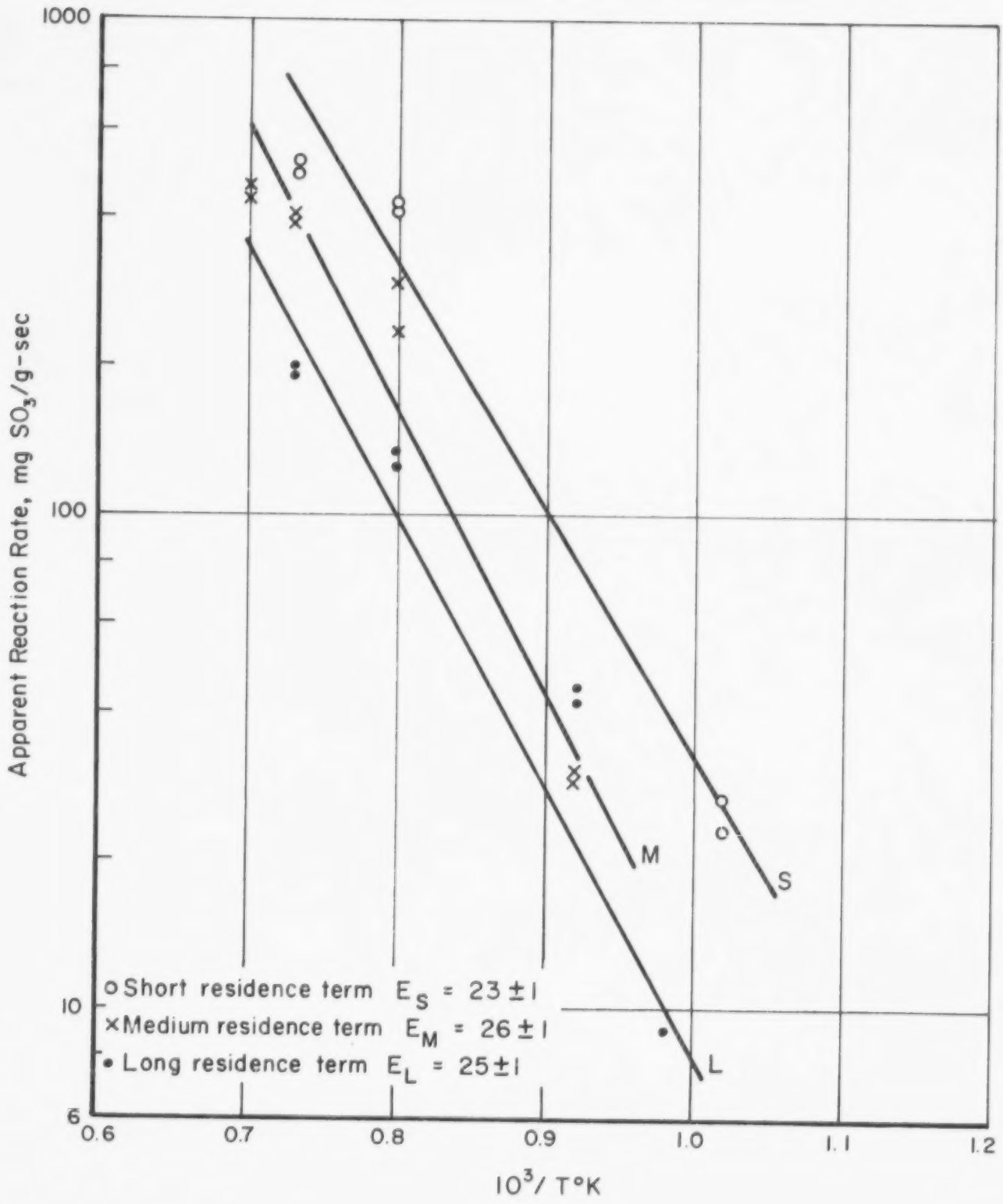

FIGURE E-1. ARRHENIUS PLOT FOR NO. 1337

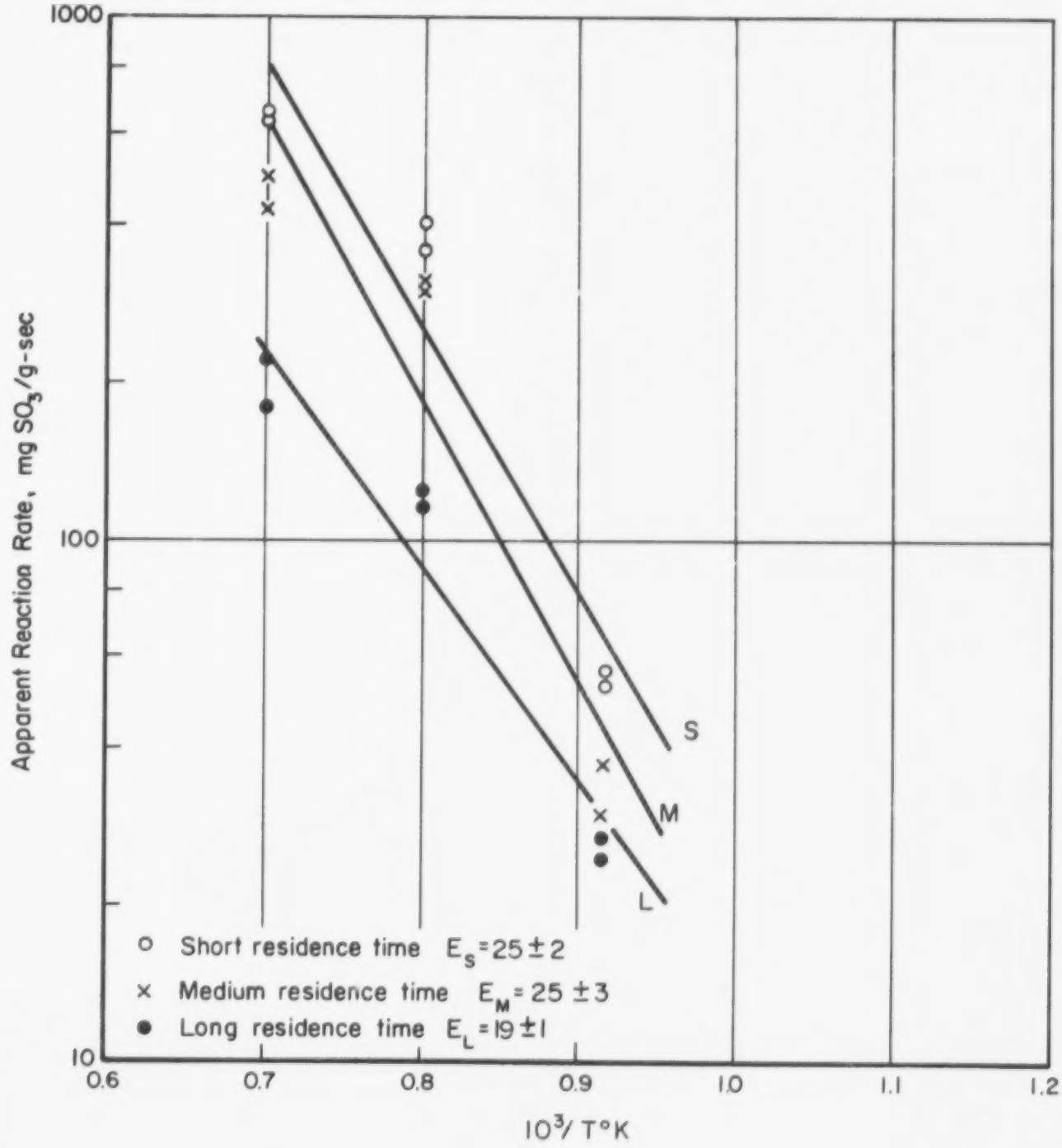

FIGURE E-2. ARRHENIUS PLOT FOR NO. 1360

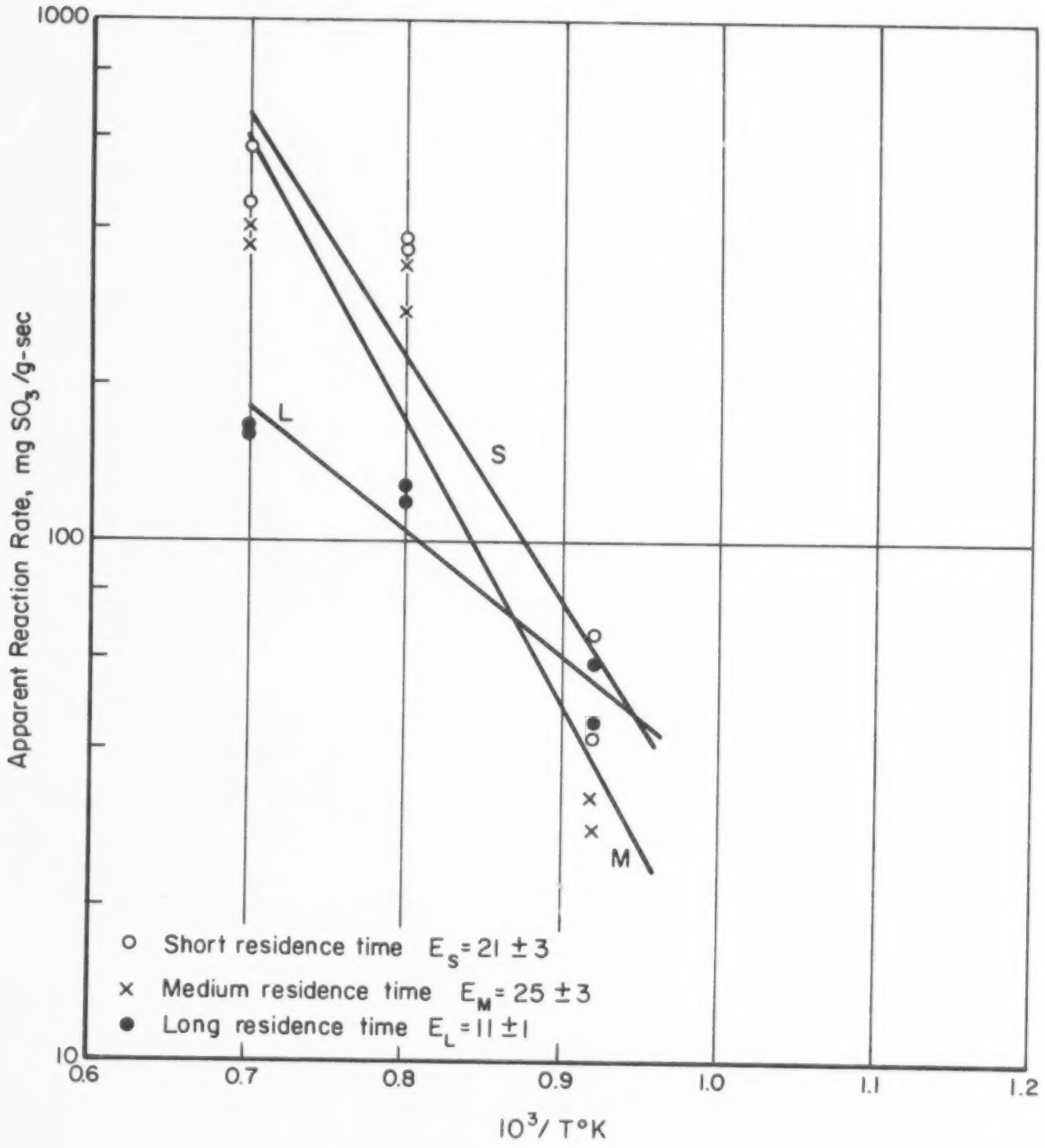

FIGURE E-3. ARRHENIUS PLOT FOR NO. 1373

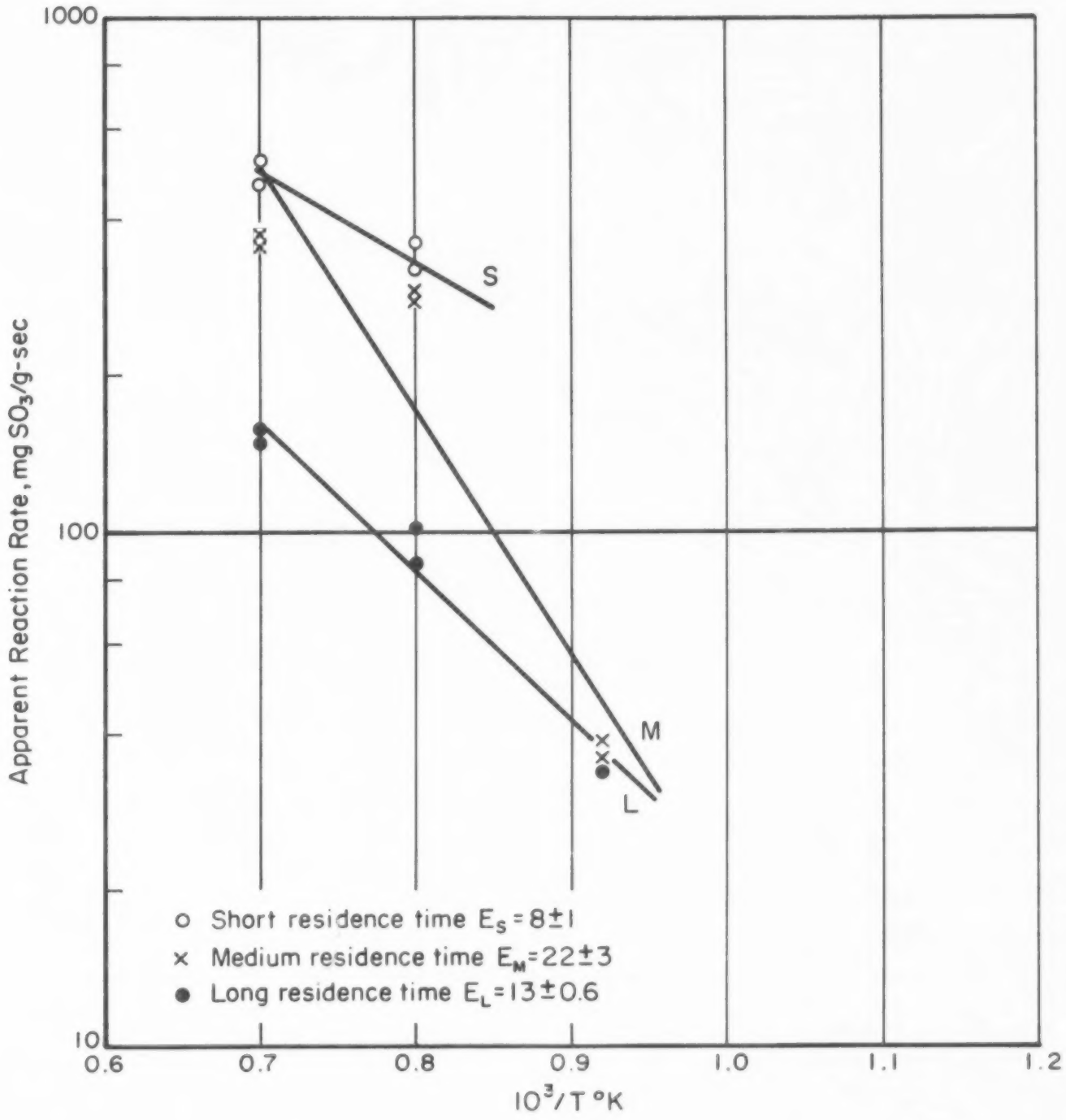

FIGURE E-4. ARRHENIUS PLOT FOR NO. 1384

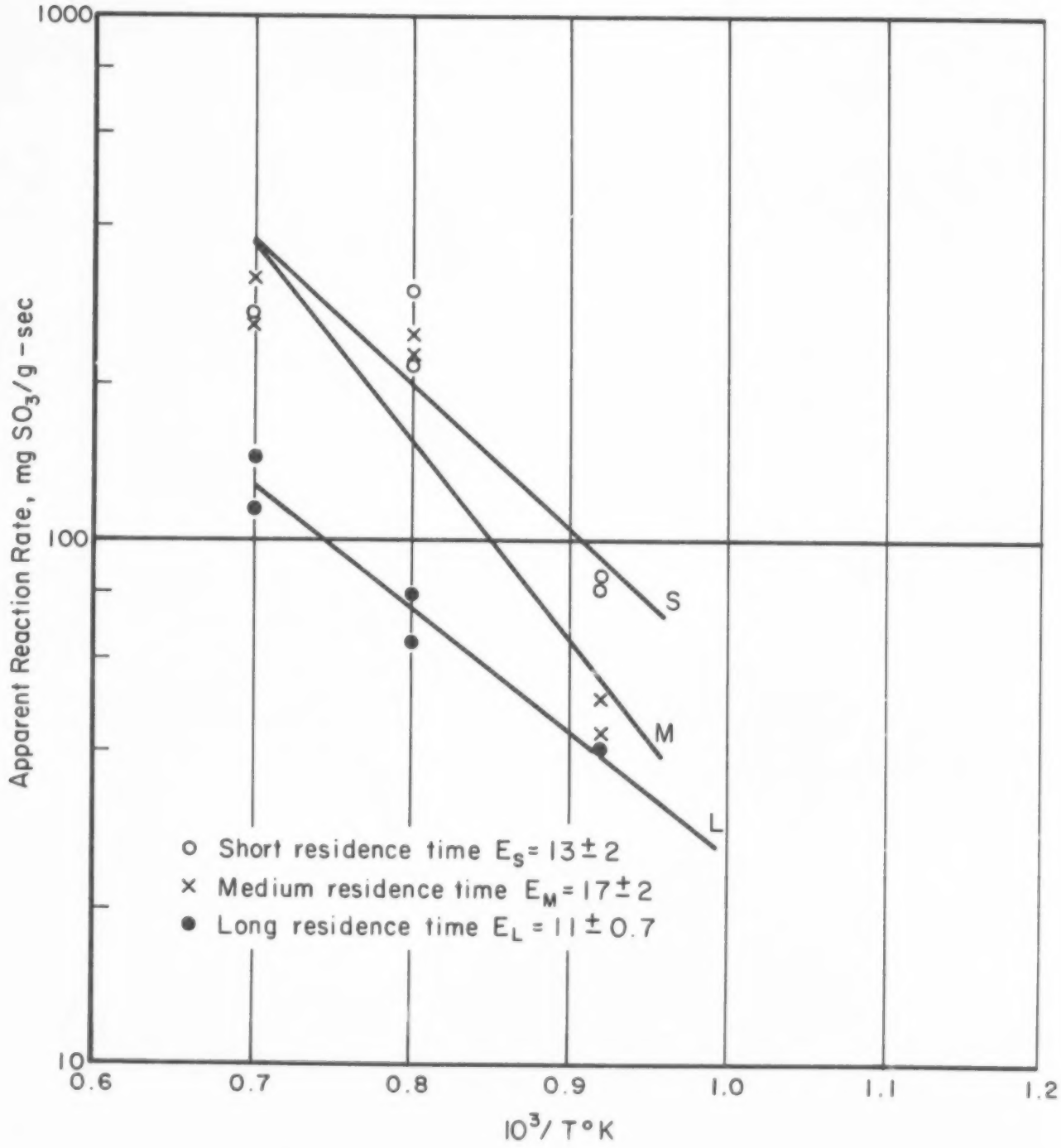

FIGURE E-5. ARRHENIUS PLOT FOR NO. 1683

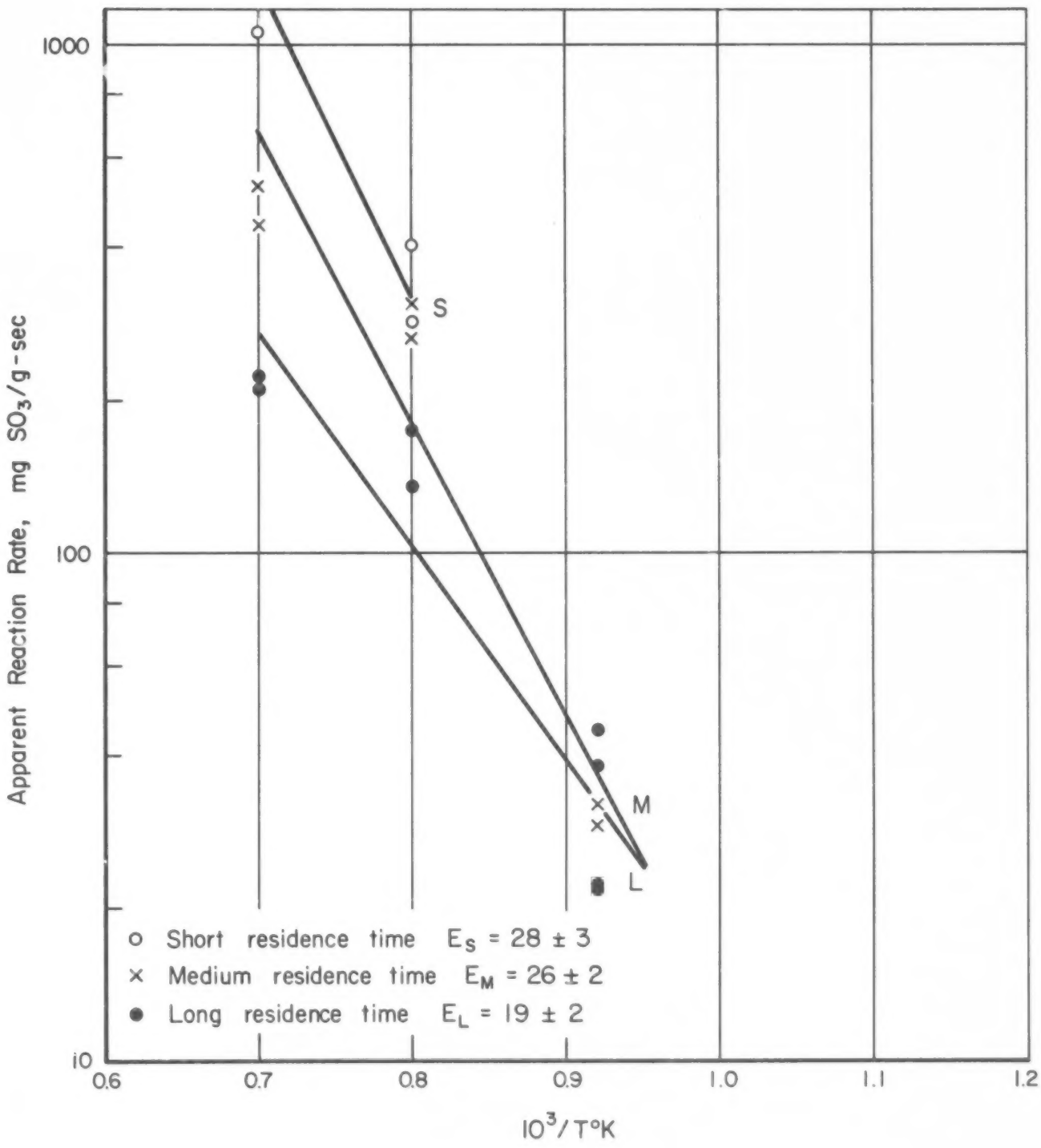

FIGURE E-6. ARRHENIUS PLOT FOR BASIC DOLOMITE

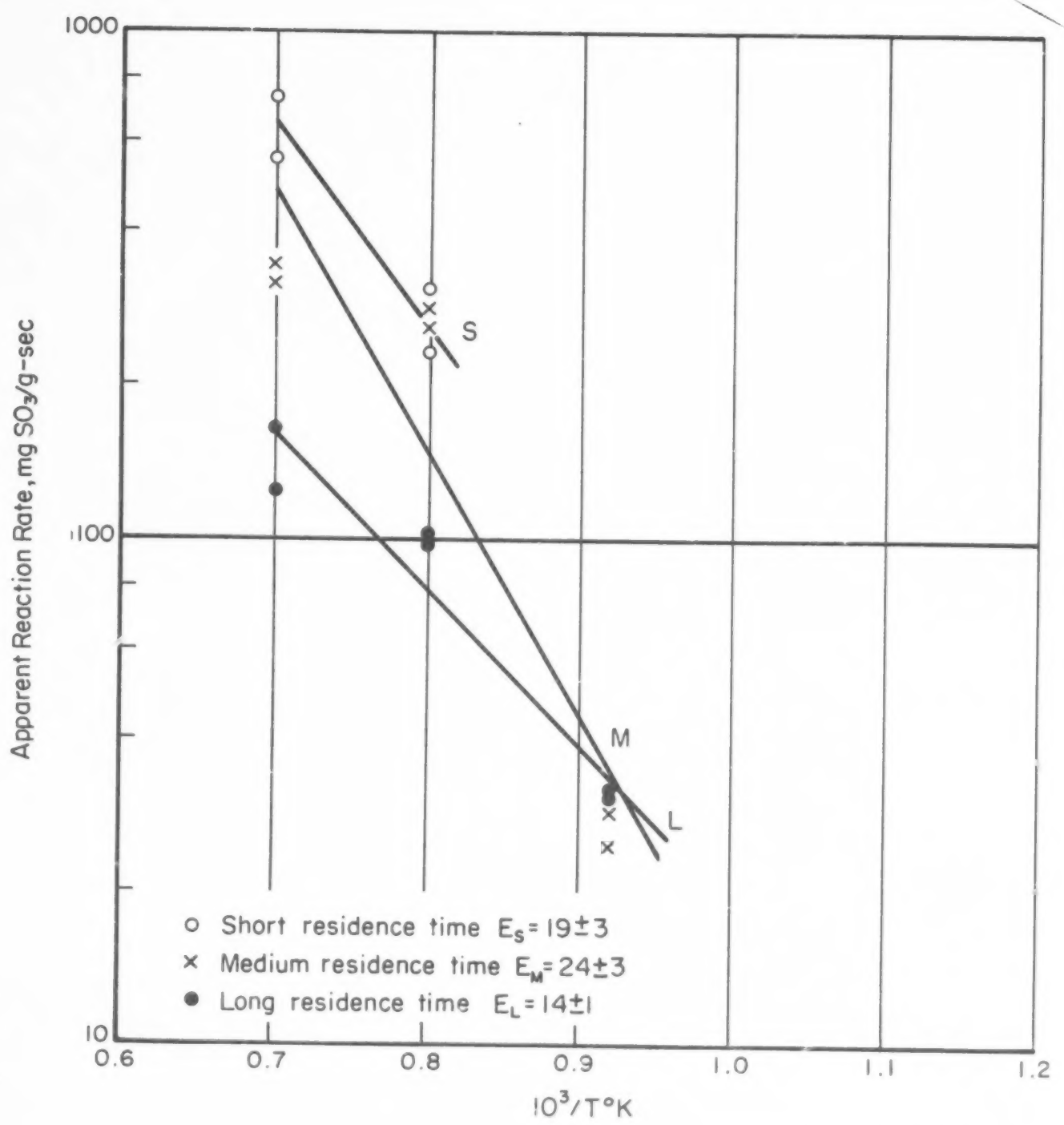

FIGURE E-7. ARRHENIUS PLOT FOR TVA LIMESTONE

APPENDIX F

INVESTIGATION OF TVA STONES

APPENDIX F

INVESTIGATION OF TVA STONES

The dispersed-phase reactor was used to study the SO_2 sorption characteristics of 15 stones under consideration for use in full-scale boiler trials by TVA. Analytical data for the stones are given in Table F-1.

Screening Program

The initial phase of this program was concerned with the screening of fifteen stones supplied by NAPCA for the purpose of selecting the five most promising materials for use in a full-scale demonstration of the dry-limestone injection process. This initial screening program was carried out using a single set of reaction conditions – 0.61 second at 2000°F in simulated flue gas containing 0.3 volume percent SO_2. The results of these screening tests are shown in Table E-2.

For most of the stones listed in Table 1, the calcium utilization was about 10 percent and the SO_3 pickup was in the range of 110 to 150 mg/g of calcine. Nos. 2060, 2064, and 2069 had SO_3 pickups above this range, and seem to be the best sorbents under the conditions employed. Nos. 2060 and 2069 also performed well in the fixed-bed tests conducted by NAPCA, but No. 2064 was one of the poorest sorbents in the fixed-bed tests. However, these tests were conducted under different conditions from those used by Battelle, and relative performance may be a function of conditions used.

Calculated values of percent calcination of the reacted stones are also shown in Table E-2. These calculated values are quite sensitive to minor variations in the accuracy of the analytical data, and values of 90 to 110 percent probably should be considered as indicating essentially complete calcination.

Because of the possible changes in ordering of stone reactivities at temperatures different from that used in the initial screening tests, five stones were selected for further examination at other temperatures to determine activation energies for the reactivity of these materials. This set of five stones was composed of the three outstanding materials listed above plus two stones, Nos. 2061 and 2062, selected by NAPCA.

Further Testing

The essence of the hypothesized model for the reaction mechanism discussed earlier in this report is that heat transfer and/or mass transport controls the rates of the two endothermic reactions (calcination of carbonate and sulfite). One consequence of this mechanism is that total sulfur pickup can go through a maximum during the initial portion of the reaction trajectory, as has been observed with samples run at different residence times under Contract No. PH 86-67-115.

TABLE F-1. SPECTROCHEMICAL ANALYSIS OF STONES[a]

Results Reported as Percent by Weight
of Ignited Sample (900 C)

Stone No.	Loss on Ignition (900°C)	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	TiO_2	SrO	Na_2O	K_2O	MnO_2
2057	43.4	1.50	<0.2	0.19	1.50	95	0.03		0.02	<0.1	<0.03
2058	43.2	2.95	0.74	0.62	6.20	89	0.05		0.04	0.10	<0.03
2059	44.1	5.10	0.63	0.64	21.3	69	0.03		0.05	0.24	<0.03
2060	41.5	8.30	1.50	0.72	6.60	81	0.07		0.09	0.31	<0.03
2061	43.4	1.40	<0.2	0.27	1.77	95	0.03		<0.02	<0.1	<0.03
2062	43.4	2.25	<0.2	0.31	2.42	94	0.03		<0.02	<0.1	<0.03
2063	43.2	1.40	0.53	0.25	1.92	95	0.05		0.05	0.13	<0.03
2064	43.3	<1.0	0.26	<0.2	0.95	96	0.03		<0.02	<0.1	<0.03
2065	43.3	1.00	0.31	<0.2	1.55	95	0.04		<0.02	<0.1	<0.03
2066	43.1	2.20	0.39	<0.2	1.13	93	0.04		0.03	<0.1	<0.03
2067	42.9	2.60	0.22	<0.2	0.08	94	0.04		0.02	<0.1	<0.03
2069	46.1	2.63	0.72	0.70	36.0	58.0	0.05		0.06	0.47	<0.03
2070	39.4	8.20	1.58	1.37	2.00	85	0.08		0.16	0.22	0.09
2071	41.2	1.83	0.59	<0.2	3.20	92	0.04		0.05	0.23	<0.03
2072	40.6	2.70	0.59	0.31	2.40	92	0.05		0.04	<0.1	<0.03

(a) Supplied by Bituminous Coal Research, Inc.

This fact had an important bearing on the manner in which the five candidate stones were tested for dependence of reactivity on temperature. As test temperatures are lowered, the maximum pickup is shifted to longer residence times. To accommodate this feature of the reaction trajectory, residence times were not held constant for runs at the various temperatures, but were lengthened as the temperature was lowered. Consequently, it is believed that the results represent similar portions of the pickup curve and it is valid to compare results obtained at various temperatures.

Test conditions, chemical analyses, and calculated values of reactivity are given in Table F-2. Apparent rates of reaction of the five stones at five temperatures are summarized in Table F-3. Arrhenius plots constructed from these data and apparent activation energies obtained by a least-squares treatment of these rates are shown in Figures F-1 to F-5. Errors indicated for the activation energies are most-probable errors obtained from the least-squares treatment. In making these calculations, all measured points were included in the computations except for the one pair of points which are obviously in error for No. 2060. It must be recognized that the values obtained are not true activation energies, since the temperatures plotted on the figures are gas temperatures; actual reaction temperatures are not known.

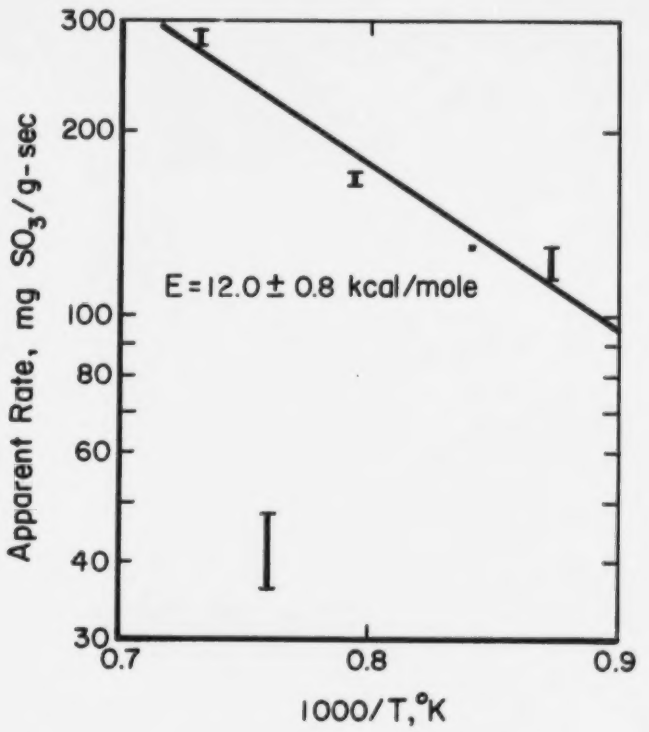

FIGURE F-1. REACTIVITY OF NO. 2060

Two of the five stones, Nos. 2064 and 2069, have high apparent activation energies and would be logical choices for trial in a boiler, providing that long-enough residence times could be achieved at higher temperatures. However, this may not be possible in the boiler if injection is made at temperatures near 2300°F, since gas temperature in a boiler drops off very rapidly below this point. If injection is made at about 2300°F, No. 2060 might be a better choice since this material has relatively high reactivity over a broad temperature range.

TABLE F-2. REACTOR DATA

Run Number	Stone Number	Gas Temp, °F	Reynolds Number	Residence Time, sec	Product Analysis, weight percent			Percent CaO Utilization	SO_3, mg per gram calcine	Calculated Percent Calcination	Gas Analysis, volume percent			
					Ca	Mg	$SO_4^{=}$(a)				SO_2	SO_3	CO_2	O_2
2-3-A	2060	1603	1920	1.43	38.8	3.7	23.7	14.2	164	60	0.302	0.0053	10.6	2.8
2-3-B	2060	1603	1920	1.43	38.2	3.7	26.4	16.1	186	62	0.302	0.0053	10.6	2.8
2-3-C	2061	1603	1920	1.43	44.9	0.4	16.9	8.8	119	55	0.302	0.0053	10.6	2.8
2-3-D	2061	1603	1920	1.43	45.0	0.4	17.4	9.0	122	56	0.302	0.0053	10.6	2.8
2-3-E	2062	1603	1920	1.43	42.9	1.7	16.4	8.9	119	47	0.302	0.0053	10.6	2.8
2-3-F	2062	1603	1920	1.43	42.9	1.8	18.6	10.1	135	50	0.302	0.0053	10.6	2.8
2-3-G	2064	1603	1920	1.43	46.0	0.4	16.0	8.1	111	56	0.302	0.0053	10.6	2.8
2-3-H	2064	1603	1920	1.43	45.8	0.4	15.1	7.7	105	54	0.302	0.0053	10.6	2.8
2-3-K	2069	1603	1920	1.43	27.5	17.5	19.5	16.5	137	32	0.302	0.0053	10.6	2.8
2-3-L	2069	1603	1920	1.43	27.2	17.0	16.9	14.4	120	23	0.302	0.0053	10.6	2.8
1-30-L	2060	1681	2000	1.29	40.6	4.5	25.4	14.5	168	72	0.303	0.0043	10.6	2.5
1-30-M	2060	1681	2000	1.29	40.6	4.9	25.1	14.4	166	71	0.303	0.0043	10.6	2.5
1-30-N	2061	1681	2000	1.29	47.8	0.4	20.0	9.7	132	69	0.303	0.0043	10.6	2.5
1-30-O	2061	1681	2000	1.29	48.3	0.4	21.2	10.2	139	73	0.303	0.0043	10.6	2.5
1-30-R	2062	1681	2000	1.29	45.3	1.8	23.1	11.9	159	66	0.303	0.0043	10.6	2.5
1-30-S	2062	1681	2000	1.29	46.3	1.7	24.4	12.2	166	71	0.303	0.0043	10.6	2.5
1-30-P	2064	1681	2000	1.29	48.1	0.4	26.3	12.7	174	77	0.303	0.0043	10.6	2.5
1-30-Q	2064	1681	2000	1.29	40.4	0.4	23.5	13.5	185	43	0.303	0.0043	10.6	2.5
1-30-T	2069	1681	2000	1.29	30.5	18.7	20.9	15.9	132	33	0.303	0.0043	10.6	2.5
1-30-U	2069	1681	2000	1.29	30.2	18.7	21.7	16.7	138	62	0.303	0.0043	10.6	2.5
1-29-A	2060	1807	2600	0.93	44.5	5.0	25.1	13.1	152	87	0.295	0.0039	10.6	2.8
1-29-B	2060	1807	2600	0.93	44.5	5.1	26.2	13.7	158	89	0.295	0.0039	10.6	2.8
1-29-C	2061	1807	2600	0.93	53.3	0.5	24.2	10.6	143	91	0.295	0.0039	10.6	2.8
1-29-D	2061	1807	2600	0.93	54.3	0.5	21.8	9.3	127	91	0.295	0.0039	10.6	2.8
1-29-E	2062	1807	2600	0.93	50.5	2.0	23.4	10.8	145	84	0.295	0.0039	10.6	2.8
1-29-F	2062	1807	2600	0.93	50.6	2.0	24.2	11.1	149	85	0.295	0.0039	10.6	2.8
1-29-G	2064	1807	2600	0.93	49.5	0.5	28.1	13.2	181	84	0.295	0.0039	10.6	2.8
1-29-H	2064	1807	2600	0.93	51.5	0.5	27.8	12.6	172	89	0.295	0.0039	10.6	2.8
1-29-J	2069	1807	2600	0.93	31.7	19.4	22.3	16.3	136	76	0.295	0.0039	10.6	2.8
1-29-K	2069	1807	2600	0.93	31.3	19.4	24.8	18.4	153	78	0.295	0.0039	10.6	2.8

TABLE F-2. (Continued)

Run Number	Stone Number	Gas Temp, °F	Reynolds Number	Residence Time, sec	Product Analysis, weight percent			Percent CaO Utilization	SO_3, mg per gram calcine	Calculated Percent Calcination	Gas Analysis, volume percent			
					Ca	Mg	$SO_4^{=(a)}$				SO_2	SO_3	CO_2	O_2
1-30-J	2060	1910	2900	0.77	45.0	4.3	28.2	3.5	27	106	0.296	0.0035	10.6	3.0
1-30-K	2060	1910	2900	0.77	45.4	4.7	27.3	4.7	37	107	0.296	0.0035	10.6	3.0
1-30-G	2061	1910	2900	0.77	55.5	0.5	21.9	9.2	125	94	0.296	0.0035	10.6	3.0
1-30-H	2061	1910	2900	0.77	55.1	0.5	21.8	9.2	125	93	0.296	0.0035	10.6	3.0
1-30-E	2062	1910	2900	0.77	53.2	1.9	21.5	9.4	126	89	0.296	0.0035	10.6	3.0
1-30-F	2062	1910	2900	0.77	52.3	1.6	23.2	10.3	139	89	0.296	0.0035	10.6	3.0
1-30-C	2064	1910	2900	0.77	53.4	0.5	26.0	11.3	155	92	0.296	0.0035	10.6	3.0
1-30-D	2064	1910	2900	0.77	52.3	0.5	22.7	10.1	138	85	0.296	0.0035	10.6	3.0
1-30-A	2069	1910	2900	0.77	32.1	19.2	23.2	16.8	139	81	0.296	0.0035	10.6	3.0
1-30-B	2069	1910	2900	0.77	32.1	19.2	25.7	18.6	154	85	0.296	0.0035	10.6	3.0
1-9-C	2057	2000	3300	0.61	54.7	0.6	23.3	9.9	134	94	0.295	0.0039	10.0	2.7
1-9-D	2057	2000	3300	0.61	53.2	0.9	21.8	9.5	129	88	0.295	0.0039	10.0	2.7
1-3-L	2058	2000	3300	0.61	53.0	3.0	24.8	10.9	138	100	0.300	0.0034	10.2	2.6
1-3-M	2058	2000	3300	0.61	50.4	3.9	28.3	13.1	166	97	0.300	0.0034	10.2	2.6
1-9-E	2059	2000	3300	0.61	37.9	13.2	22.0	13.5	133	80	0.295	0.0039	10.0	2.7
1-9-F	2059	2000	3300	0.61	38.4	13.3	21.1	12.8	126	81	0.295	0.0039	10.0	2.7
1-9-L	2060	2000	3300	0.61	47.3	3.5	29.2	14.4	166	103	0.295	0.0039	10.0	2.7
1-9-M	2060	2000	3300	0.61	47.6	3.1	31.4	15.3	178	107	0.295	0.0039	10.0	2.7
1-3-N	2061	2000	3300	0.61	56.6	0.5	24.7	10.1	138	100	0.300	0.0034	10.2	2.6
1-3-O	2061	2000	3300	0.61	55.4	0.6	25.9	10.9	148	99	0.300	0.0034	10.2	2.6
1-9-G	2062	2000	3300	0.61	56.4	1.5	25.1	10.3	139	101	0.295	0.0039	10.0	2.7
1-9-H	2062	2000	3300	0.61	54.7	1.7	24.1	10.2	138	96	0.295	0.0039	10.0	2.7
1-9-J	2063	2000	3300	0.61	57.6	0.7	21.1	8.5	116	99	0.295	0.0039	10.0	2.7
1-9-K	2063	2000	3300	0.61	58.2	0.7	24.7	9.9	134	104	0.295	0.0039	10.0	2.7
1-9-N	2064	2000	3300	0.61	53.1	0.4	31.3	13.7	188	98	0.295	0.0039	10.0	2.7
1-9-O	2064	2000	3300	0.61	53.3	0.4	31.9	13.9	191	99	0.295	0.0039	10.0	2.7
1-3-G	2065	2000	3300	0.61	57.8	0.7	21.6	8.7	118	100	0.300	0.0034	10.2	2.6
1-3-H	2065	2000	3300	0.61	57.2	0.6	24.0	8.8	119	98	0.300	0.0034	10.2	2.6
1-3-E	2066	2000	3300	0.61	56.1	0.8	25.4	10.5	140	103	0.300	0.0034	10.2	2.6
1-3-F	2066	2000	3300	0.61	56.3	0.7	24.5	10.1	134	102	0.300	0.0034	10.2	2.6

TABLE F-2. (Continued)

Run Number	Stone Number	Gas Temp, °F	Reynolds Number	Residence Time, sec	Product Analysis, weight percent			Percent CaO Utilization	SO_3, mg per gram calcine	Calculated Percent Calcination	Gas Analysis, volume percent			
					Ca	Mg	$SO_4^{=(a)}$				SO_2	SO_3	CO_2	O_2
1-9-A	2067	2000	3300	0.61	54.0	0.7	23.8	10.2	138	94	0.295	0.0039	10.0	2.7
1-9-B	2067	2000	3300	0.61	53.4	0.5	24.0	10.5	140	93	0.295	0.0039	10.0	2.7
1-3-A	2069	2000	3300	0.61	30.2	18.4	27.9	21.5	178	75	0.300	0.0034	10.2	2.6
1-3-B	2069	2000	3300	0.61	31.8	20.0	27.4	20.0	166	86	0.300	0.0034	10.2	2.6
1-3-C	2070	2000	3300	0.61	53.0	1.0	26.1	11.5	139	108	0.300	0.0034	10.2	2.6
1-3-D	2070	2000	3300	0.61	53.3	1.0	27.9	12.1	148	111	0.300	0.0034	10.2	2.6
1-3-P	2071	2000	3300	0.61	52.9	2.9	22.2	9.8	128	92	0.300	0.0034	10.2	2.6
1-3-Q	2071	2000	3300	0.61	52.5	2.9	24.0	10.6	140	93	0.300	0.0034	10.2	2.6
1-3-J	2072	2000	3300	0.61	56.1	1.2	23.5	9.7	128	102	0.300	0.0034	10.2	2.6
1-3-K	2072	2000	3300	0.61	54.4	1.1	26.2	11.2	147	100	0.300	0.0034	10.2	2.6

(a) Expressed as $CaSO_4 \cdot 2H_2O$.

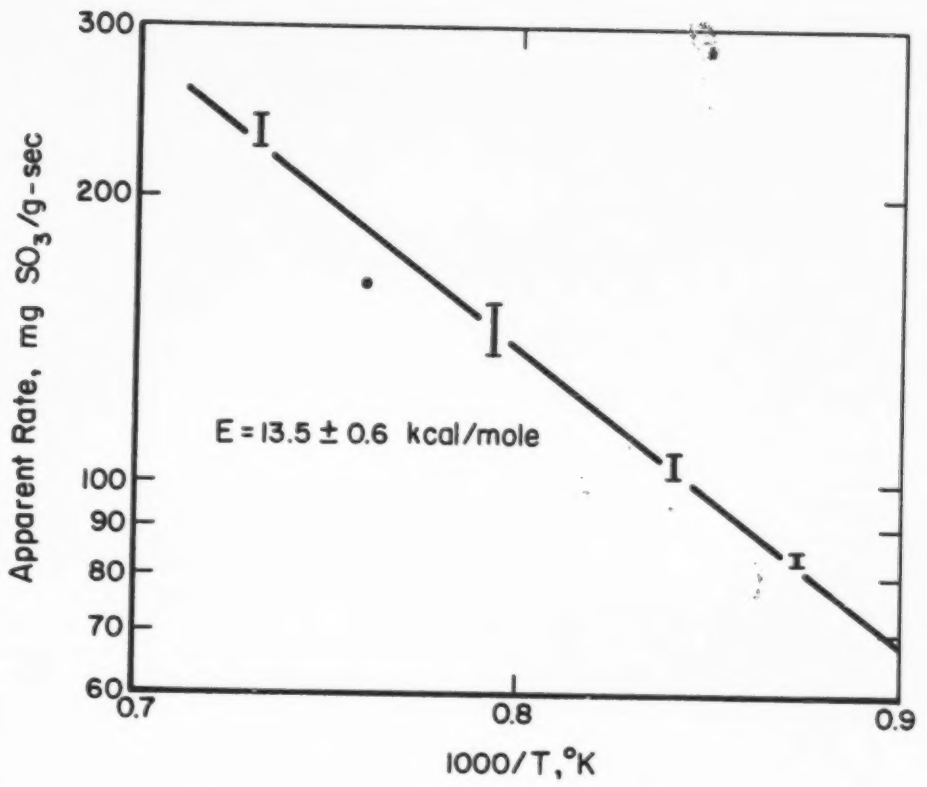

FIGURE F-2. REACTIVITY OF No. 2061

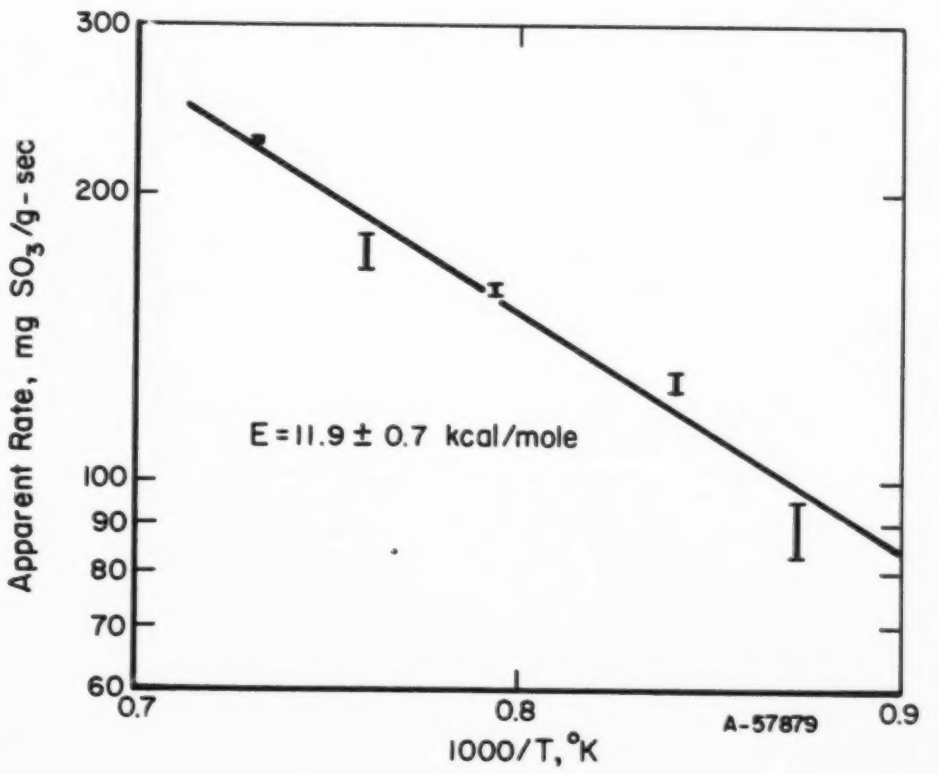

FIGURE F-3. REACTIVITY OF No. 2062

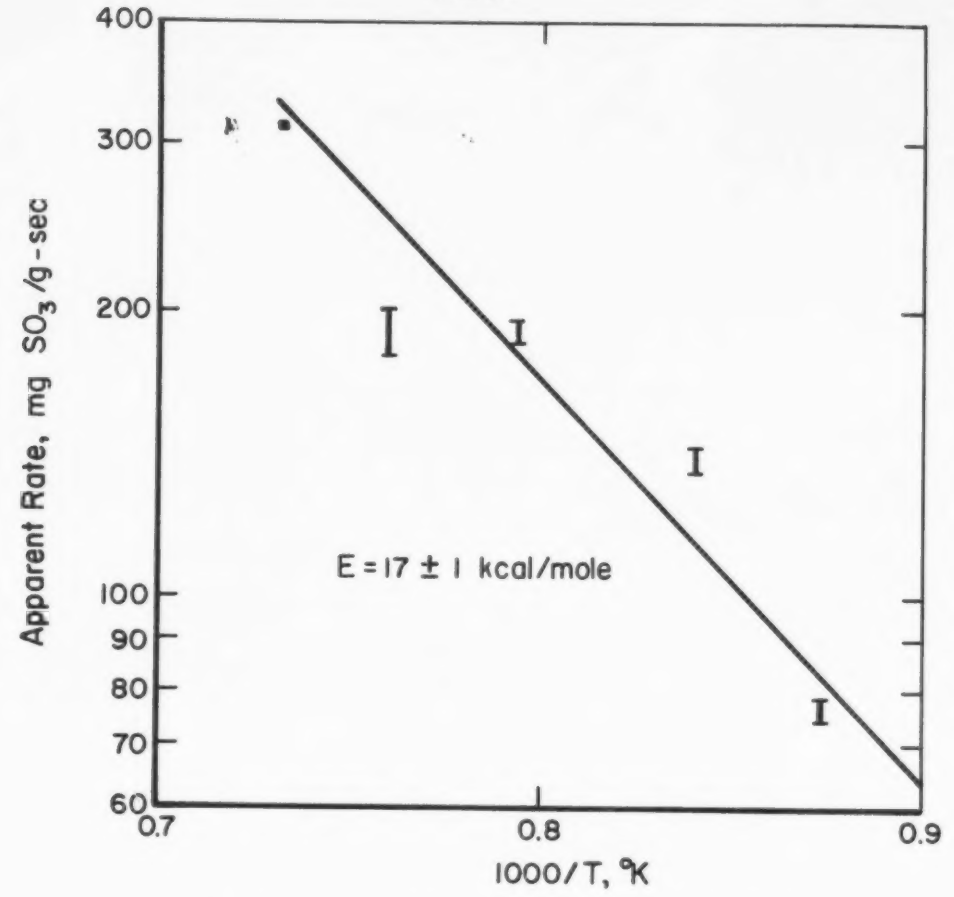

FIGURE F-4. REACTIVITY OF No. 2064

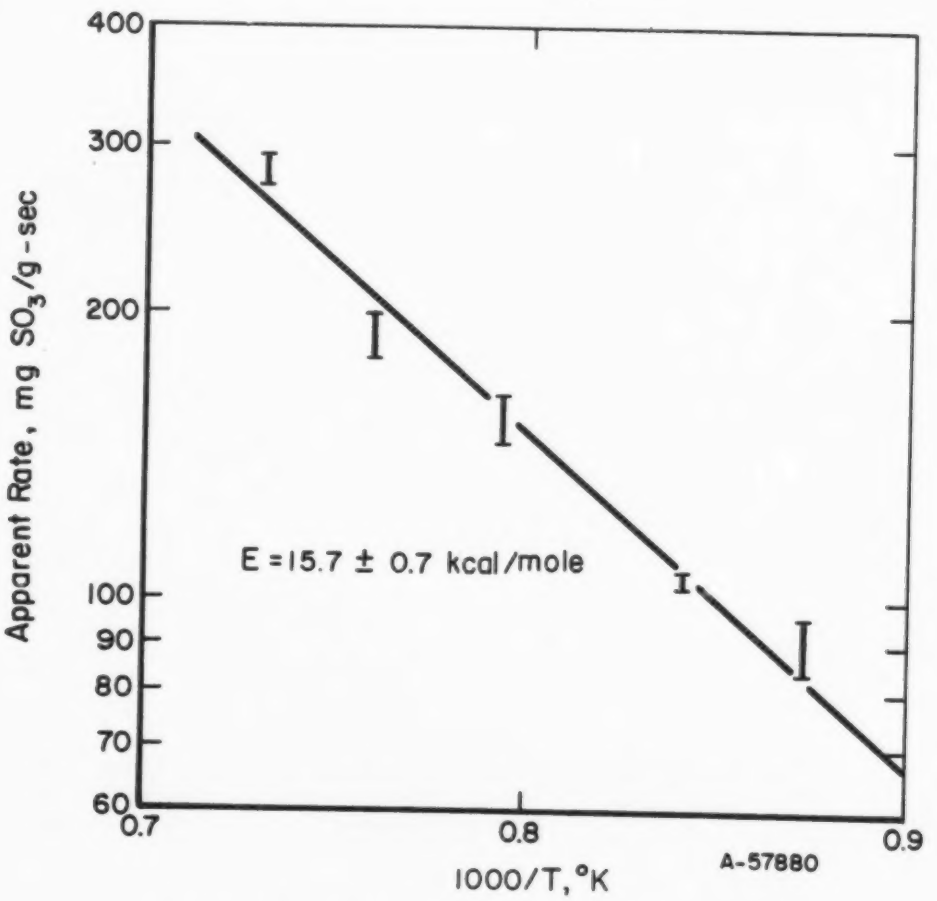

FIGURE F-5. REACTIVITY OF No. 2069

The current work emphasizes the need for further development of means for relating the results obtained in the dispersed-phase reactor to the performance of a stone in a boiler. In particular, a model of the reaction system which takes into account the differences in the thermal history of a stone particle in boiler and reactor environments is needed.

TABLE F-3. SUMMARY OF APPARENT REACTION RATES(a)

	Temperature and Residence Time				
Stone No.	1603°F 1.48 sec	1681°F 1.29 sec	1807°F 0.93 sec	1910°F 0.77 sec	2000°F 0.61 sec
2060	122 ± 8	129 ± 1	167 ± 3	42 ± 6	282 ± 10
2061	84 ± 1	105 ± 3	145 ± 9	162 ± 0	234 ± 8
2062	89 ± 6	126 ± 3	158 ± 2	172 ± 8	227 ± 1
2064	76 ± 2	139 ± 4	190 ± 5	190 ± 11	311 ± 2
2069	90 ± 6	105 ± 2	155 ± 9	190 ± 10	282 ± 10

(a) mg SO_3/g-sec.